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EQUILIBRIA IN SYSTEMS CONTAINING ALCOHOLS, SALTS AND WATER, INCLUDING A NEW METHOD OF ALCOHOL ANALYSIS

BY

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CONTENTS

EQUILIBRIA IN SYSTEMS CONTAINING ALCOHOLS, SALTS AND WATER, INCLUDING A NEW METHOD OF ALCOHOL ANALYSIS[1]

In the course of some work involving potassium fluoride, it was observed that this substance would salt out ethyl alcohol from aqueous solution, and that it possessed this property over a very wide range of concentrations of alcohol and salt. The solid salt extracts quite a good deal of water from ordinary "95 per cent" alcohol, forming either two liquid layers, or a mass of crystals overlaid by a layer of stronger alcohol. In contrast to the behavior of potassium carbonate, this dehydration appeared to take place in a very short time, and it was thought that potassium fluoride might become technically useful as a dehydrating agent for alcohol and similar organic liquids. It was also thought that its salting-out powers might make possible a new rapid method for the determination of alcohol, which would have advantages over the specific gravity determination in point of speed, independence of weather conditions and adaptability to determinations where the direct determination of specific gravity would be impossible or inaccurate.

It is well known that the higher alcohols, acetone, and many other organic liquids can be precipitated from their aqueous solutions by addition of various salts. Potassium carbonate seems to be the only substance which is capable of salting out methyl alcohol,[2] while the carbonates and hydroxides of sodium and potassium, sulphates of sodium, ammonium, cadmium, manganese, iron (ferrous), cobalt, nickel, magnesium and zinc, alum, sodium phosphate, thiosulphate and silicate, potassium phosphate, citrate and nitrate, ammonium nitrate and ammonium citrate[3] are all capable of producing two layers in solutions of ethyl alcohol under certain conditions. The phenomenon of salting out, or the formation of layers, is not confined exclusively to organic compounds in water solution, as Proctor[4] found that ammonia is salted out and forms two layers with a strong solution of either potassium carbonate or sodium silicate. Newth[5] recently rediscovered the salting-out of ammonia by the carbonate.

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[1] An abstract of this paper was published in the Proceedings of the Eighth International Congress of Applied Chemistry, vol. 22.

[2] Linebarger, Am. Chem. J., 1892, **14**, 380.

[3] Firnhaber, Archiv des Apothekervereins Norddeutschland, 1824, **7**, 151; Linebarger, loc. cit., Brandes, Pogg. Ann., **20**, 586; Schiff, Lieb. Ann., **118**, 362; Proctor, Chem. News, 1864, **9**, 25; Parmentier, Compt. rend., **104**, 686; Traube und Neuberg, Z. physik. Chem., 1887, **1**, 509; Bodländer, Z. physik. Chem., **7**, 308; Dodge and Gratton, J. physic. Chem., 1898, **2**, 498; de Bruyn, Z. physik. Chem., 1900, **32**, 64; Ketner, Z. physik. Chem., 1902, **39**, 641; Fleckenstein, Physikal. Zeit., 1905, **6**, 419.

[4] loc. cit.

[5] J. Chem. Soc., 1900, **77**, 775.

The dehydration of alcohol by various chemical compounds has been studied by many chemists.[1] Of the various substances used, the commonest is lime, which gives an alcohol of nearly 100 per cent. It causes, however, a large loss in alcohol, and is inconvenient on account of the large quantities of lime (0.55 kg. per liter, according to Kailan) required. The general theory of the drying action of a salt on a liquid, and the importance of choosing a salt which takes up a large per cent of its weight in water have been discussed by Foote and Sholes.[2] Of the salts which can give a product containing over 97 per cent alcohol, lime takes up 32 per cent of its weight of water, anhydrous copper sulphate 11 per cent, anhydrous zinc sulphate 11 per cent, magnesium sulphate 15 per cent, anhydrous barium chloride 7.7 per cent, and anhydrous potassium carbonate 13 per cent. According to the results of Foote and Sholes, the lowest hydrates of these substances are in equilibrium with 99.5, 99.5, 99.4, 99.4, 98.4, and 99.3 per cent alcohol, respectively, at 25°. At boiling temperatures, however, Kailan found that he could get 99.9 per cent alcohol by the use of lime. Potassium fluoride, absorbing 62 per cent of its weight of water to form the lowest hydrate, and being in equilibrium at this point with 97.5 per cent alcohol, according to work described herein, certainly deserves to rank well among drying agents for liquids miscible with water, and by virtue of the speed with which it absorbs this water, it has many advantages over lime and potassium carbonate, which are notoriously slow to reach equilibrium. Foote and Sholes state that the equilibrium with magnesium sulphate was reached very slowly, and experience with copper sulphate will convince any one that it is not a rapid dehydrating agent. Calcium carbide, calcium, aluminum and magnesium and their amalgams have been used to remove the last trace of water.

Among organic chemists, it is quite common to dry certain liquids over a saturated solution of potassium carbonate. This has the advantage over the use of the solid salt that the loss of liquid, mechanically, is less, and it is much quicker. Any salt which would be suitable for this purpose must have a decided "salting-out" power, and its saturated solution must have a low vapor tension. With the exception of potassium carbonate, and the hydroxides of sodium and potassium, none of the salts named above as able to salt out alcohol are deliquescent, so that their hydrates, not to speak of their saturated solutions, have relatively large vapor tension. By plotting the results of Foote and Sholes, the curve shown in figure 1 is obtained,

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[1] Soubeiran, Ann., 1839, **30**, 356; Mendeleef, Z. f. Chem., 1865, 260; Erlenmeyer, Ann., **160**, 249; Smith, Chem. News, **30**, 235; Lescoeur, Bull. soc. chim., 1897, (3), **17**, 18; Yvon, Compt. rend., 1897, **125**, 1181; Ostermeyer, Pharm. Zeit., **43**, 99; Z. anal. Chem., 1900, **39**, 654; Vitali, Boll. chim. farm., **37**, 257; Z. anal. Chem., 1900, **39**, 46; Bull, Chem. Zeit., 1900, **24**, 814, 845; Young, J. Chem. Soc., 1902, **81**, 707; Evans and Fetsch, J. Am. Chem. Soc., 1904, **26**, 1158; Winkler, Ber., 1905, **38**, 3612; Elektrochem. Werke Bitterfeld, Brit. Pat., 31,567, Sept., 1906, and Ger. Pat., 175,780, Sept., 1905; Klason and Norlin, Arkiv. Kem. Min. Geo., 1906, **2**, 1, J. Chem. Soc., 1906, **90**, i, 921; Kailan, Monatsh., 1907, **28**, 927; Plücker, Z. Nahr. Genussm., **17**, 454; Pozzi-Escot, Bull. assoc. chim. sucr. dist., **26**, 580; Hess, U. S. Pat. 996,763; Chem. Fabr. Griesheim Elektron, Ger. Pat. 236,591; Foote and Sholes, J. Am. Chem. Soc., 1911, **33**, 1309.

[2] loc. cit.

showing the vapor tension of the water in strong alcohol. The solutions of alcohol with which saturated solutions of potassium carbonate and fluoride and the solid hydrates are in equilibrium, when plotted on this curve give

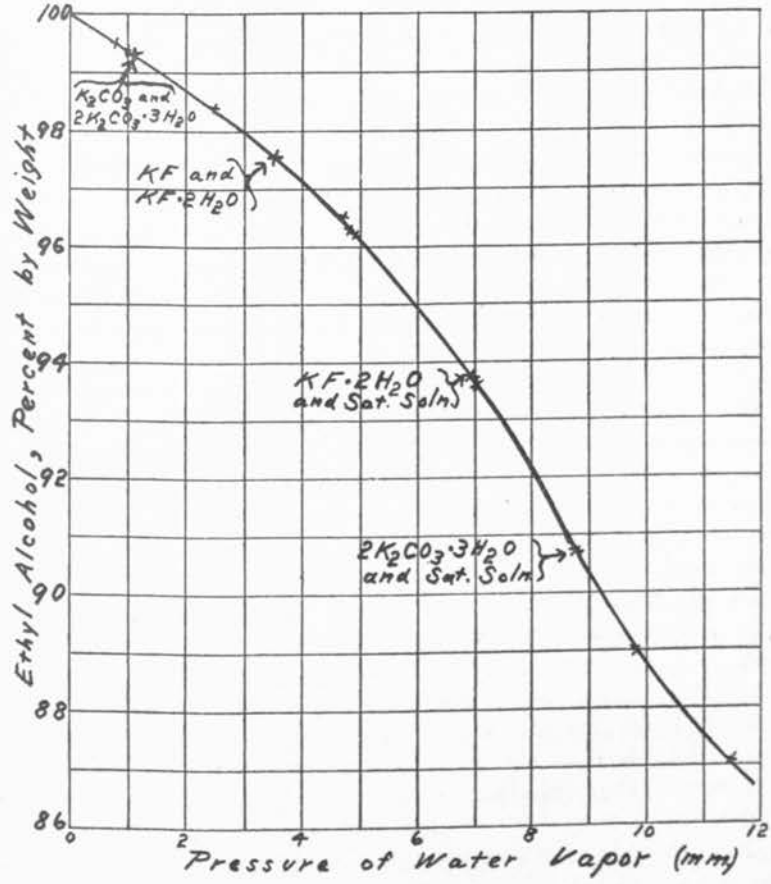

Figure 1. Equilibrium between Alcohol, Water Vapor, and Salts.

the approximate value of their vapor tension. It will be seen that while the vapor tension of the hydrate of potassium carbonate is lower than that of the hydrate of the fluoride, the saturated solution of the latter has a lower vapor tension than that of the former, and hence is a better drying agent. From this curve it appears that, neglecting the effect of the small amount of dissolved potassium fluoride on the vapor tension of the alcohol, the vapor tension of the saturated solution of the fluoride is 6.9 mm, and that of the solid hydrate 3.5 mm.

The fact that potassium fluoride "salts out" alcohol from aqueous solution seems never to have been mentioned in the literature, although it must

have been noticed by Berzelius[1] who first described the salt, and was amazed by its power to slowly etch glass. He attempted to extract the free acid which he supposed must be present, by shaking the concentrated solution with alcoholic potash, but found the salt unchanged by this treatment. Rose[2] must also have noticed the salting out, as he tried to separate the fluoride into an acid salt and free potash by recrystallization, and when this did not work, by precipitation with alcohol. He speaks of treating a very concentrated solution of the salt with strong alcohol, "by which only potassium fluoride containing water was precipitated, while a very small amount of potassium fluoride remained dissolved in the alcohol." He is evidently speaking of the precipitation of the hydrate in crystalline form, as he says again, after speaking of the difficulty of obtaining the hydrate in crystalline form from an aqueous solution by ordinary means: "This (hydrate) is obtained more easily if one adds strong alcohol to a concentrated solution of potassium fluoride. Only a little of the salt is dissolved, the greater part of it precipitates in a hydrated form (im wasserhaltigen Zustand)." He determined the percentage of water in the hydrate, mentioning especially that two samples were precipitated by alcohol and dried between filter papers. His analyses indicate that he was working with the hydrate $KF.2H_2O$, which has since been analysed and identified as the only one formed at ordinary temperatures, by Guntz,[3] Fremy,[4] Mylius and Funk[5] and de Forcrand.[6] The latter author has also shown the existence of a hydrate $KF.4H_2O$, formed below 20°, and melting at 19.3°, while the other hydrate melts at 41°. The person who comes the nearest to mentioning the salting-out power of this salt is Carnot,[7] who in purifying some of it, mentions adding strong alcohol to the solution until a slight cloudiness appears, allowing to stand, and filtering, apparently for the purpose of removing fluosilicates.

Aside from the work above-mentioned, there is very little literature on the properties of the neutral potassium fluoride or its solutions, and none on its preparation.[8] It would seem that very few people have ever used it, and it is not listed in most chemical price-lists.

The precipitation of a liquid from water by the addition of a salt comes under that general class of equilibria in ternary mixtures where two liquid phases are possible. The general theory of such systems, and the form of the isotherms obtained, have been very thoroughly discussed by Schreinemakers.[9] There are four classes into which such equilibria are divided: (1) each of the three components forms a binary system having two liquid phases when mixed with either of the other components, (2) two liquid

[1]Pogg. Ann., **1**, 11. [2]Pogg. Ann., 1842, **55**, 538. [3]Ann. chim. phys., (6), **3**, 17.
[4]Ann. chim. phys. (3), **47**, 27. [5]Ber., 1897, **30**, 1716. [6]Compt. rend., **152**, 1073.
[7]Bull. soc. chim., (3), **9**, 71.
[8]F. W. Clarke, Am. J. Sci., (3), **13**, 291; Kohlrausch, Wied. Ann., 1879, 1; Guntz, Compt. rend., **97**, 256; Tamman, Wied. Ann., **24**, 530; Petersen, Z. phys. Chem., **4**, 384; Ditte, Compt. rend., 1896, **123**, 1281; 1897, **124**, 29; Pauli, Z. Elektrochem., 1897, **3**, 474; Tanatar, Z. anorg. Chem., 1901, **28**, 255; Fox and Herz, Z. anorg. Chem., 1903, **35**, 129; Karadeef, Centr. Min., 1909, 728; C. A., 1911, **4**, 433.
[9]Z. phys. Chem., 1897, **22**, 93, 515; **23**, 649.

phases are found in two of the possible binary systems above-mentioned but not in the third, (3) in only one of the binary systems can two liquid layers appear, (4) each component, mixed with either of the others, gives a system with only one liquid phase, i. e., a solution of one in the other, and only when all three are present can two liquid phases exist. All the above classes refer to stable systems only, all four are realizable experimentally, and examples of each have been studied. The salting-out of the alcohols here studied comes under the fourth class, since neither in the system alcohol-water, alcohol-salt (free from water) nor water-salt can two liquid layers

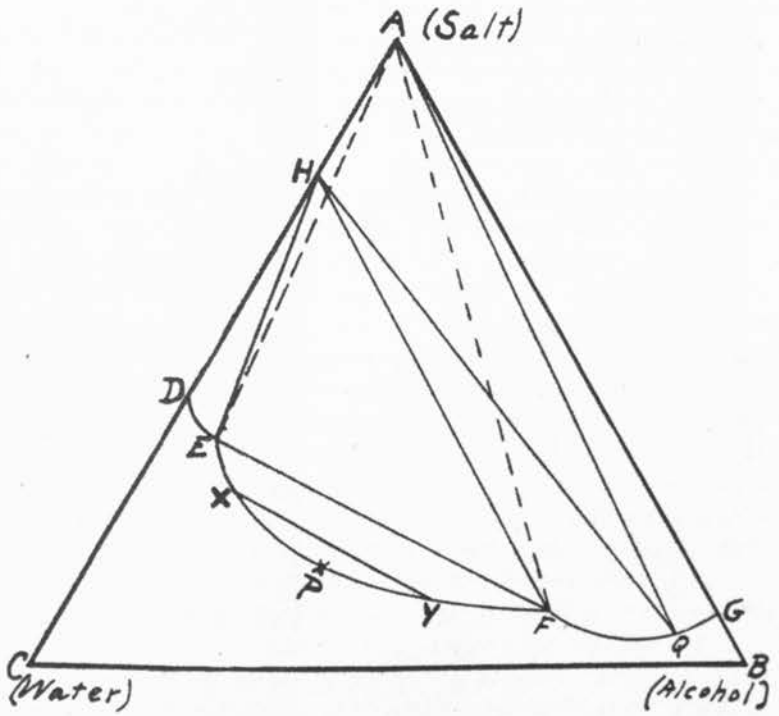

Figure 2. General form of the Isotherms in a Ternary System of the Fourth Class.

be formed, but when all three are present in certain proportions such layers are formed within certain limits of temperature.

In representing ternary systems, Schreinemakers and others have employed a system of co-ordinates founded on the equilateral triangle. If the three vertices of the triangle ABC (fig. 2) represent the three pure components, points on the side AB of the triangle represent mixtures of the two substances A and B, while any point within the triangle represents a mixture containing all three substances. In plotting such a

point, distances are measured parallel to the sides of the triangle, the distance thus measured to any side showing the per cent of the component which is represented by the vertex opposite to that side. Since the sum of such distances is equal in length to a side of the triangle, such sum is 100 per cent, and any possible percentage composition of the mixture can be represented by a point within the triangle, and every point within the triangle represents a possible mixture of all three components. In such a triangle there will always be a line which marks the boundary between the homogeneous and heterogeneous systems. In the case which we are considering, where one of the components is a solid, this curve at a given temperature will in general consist of three parts:

(1) a line DE (fig. 2) starting from the point D which represents the composition of a saturated solution of the salt in water, and running to that point E within the triangle, which represents the composition of the lower of the two liquid layers which are in equilibrium with the hydrate of the salt (if it forms one at that temperature). This point may be considered to be that saturated solution of the salt in water, which has then been saturated with alcohol. In general, the addition of the alcohol reduces the percentage of the salt in the mixture, by precipitation of part of the salt. This point E then represents a saturated solution of salt in water, in which part of the salt has been replaced by alcohol until the further addition of alcohol produces no change in the composition of the solution.

(2) From this point E a line EPF runs to the point F representing the composition of the upper layer (alcoholic solution of the salt and water) which is in equilibrium with the solution at E, and also with the hydrate of the salt (or the anhydrous salt, if no hydrate exists under the given conditions). The point at which these two solutions co-exist is a quadruple point, since four phases (a solid, two liquids and a vapor) are present. Since there are but three components in the four phases, the system at this point has but one degree of freedom, i. e., at a given temperature the system is invariant, and the conjugate solutions (E and F) can each have only one definite composition.

(3) From the point F representing the composition of the upper layer at the quadruple point, a line runs to the point G representing the composition of the saturated solution of the salt in the alcohol.

In general each of these three lines is concave toward the vertex representing the salt. The line DE is the locus of all aqueous solutions saturated with respect to the salt, and of alcoholic content varying from none to the maximum possible in the saturated salt solution (at the quadruple point E). The line EPF, commonly called the binodal curve, is the locus of all conjugate solutions; i. e., if we have two liquid phases in the system at the given temperature, the composition of each will be represented by a point on this line, as X and Y. The line FG represents the solubility of the salt and its

various hydrates in alcohol-water mixtures from the composition represented at F to absolute alcohol.

In figure 2, mixtures represented by points within the area DEPFGBC are homogeneous, those within the area HDE (if H be the point representing the composition of the hydrate of the salt which is stable at that temperature) will consist of a mixture of the solid hydrate and a solution having a composition represented by some point on the line DE. A mixture lying within the triangle HEF will consist of the solid hydrate and the two solutions represented by points E and F, which by definition are the only two solutions which can be in equilibrium with the solid hydrate when both water and alcohol are present in sufficient quantity to give two liquid phases. Mixtures within the area EPF will consist of two conjugate solutions whose composition will be represented by two points on the binodal curve EPF. The point P is the "plait point," i. e., the point of union of the two branches of the binodal curve which represent the composition of the upper and lower layers respectively. To state it from another view-point, a mixture whose composition was represented by the point P, would be homogeneous, but the addition of an infinitesimal portion of the salt would cause it to separate into two layers having compositions represented by points on the binodal curve lying very close to P, one a little to the right and the other a little to the left. By determining analytically the composition of two conjugate solutions X and Y, and calculating the composition of the mixture containing varying quantities of each, it may be shown that the locus representing such mixtures is the straight line XY, which is called a tie-line.

Any mixture whose composition is represented by a point within HFQ will separate into the solid hydrate and a solution lying along FQ, where Q represents the composition of the alcoholic solution which is in equilibrium with both the hydrate and the anhydrous salt. This is the solution to which the anhydrous salt dehydrates weaker alcohol. The triangle AHQ contains all mixtures of the hydrate and anhydrous salt in equilibrium with alcoholic solution Q. The area AQG consists of mixtures of the anhydrous salt and alcoholic solutions of it having a composition represented by a point on line QG.

If the salt does not form a hydrate, the point H may be considered as moving along CA to coincide with A, while Q moves along BF and coincides with F as indicated by the broken lines. Area AHFQ disappears entirely, as it is the area over which the hydrate existed in equilibrium with an alcoholic solution of itself, and H becomes A and Q becomes F in the above discussion.

EXPERIMENTAL METHODS

The Binodal Curve. The point at which an inhomogeneous solution of the salt, alcohol and water just becomes homogeneous is a point on the binodal curve, and the determination of a number of such points enables one to plot this curve accurately. Such points were determined for the different alcohols and salts as follows: An Erlenmeyer flask with a well-ground glass stopper was cleaned, dried and weighed. With potassium fluoride, the salt was ignited in a weighed, covered platinum crucible; weighed, as much as possible transferred to the flask, and the rest rinsed into the flask with distilled water. In this way the weight of the anhydrous salt was accurately obtained, as an experiment showed that with the crucible covered, in the dry winter air of this climate, the increase in weight during seven minutes in the open air was only .0007 gm. In the case of large weights of the fluoride, this precaution was considered unnecessary, as the possible percentage error was negligible; the salt was then weighed in the stoppered flask, as was also done in the case of the other salts. The salt was next dissolved in distilled water, and the whole weighed. Enough alcohol to form two liquid phases was then added, together with a trace of the solid dye used as an indicator. The flask was again weighed, water added from a burette until the solution just became homogeneous and clear, the flask weighed again, and the addition of alcohol and water repeated until a series of results was obtained.

All weighings of solutions were made on a large Sartorius balance, of ample carrying capacity, and easily sensitive to 0.5 mg. with a load of 500 grams on each pan, but no attempt was made to weigh closer than the nearest milligram. It is not claimed that the end-point of the titration could generally be determined closer than 0.1 to 0.2 gm. water, but it was thought best to weigh to milligrams to minimize cumulative errors in the amounts of water and alcohol present. When a solution had to stand long enough between determinations to lose weight appreciably, the loss was determined as noted in the tables, and divided between the alcohol and water in proportion as each was present. This was done on the theory that the loss was caused by evaporation of the solution which was in the ground joint. Such loss was usually less than 30 mg. None of the flasks used showed any signs of the slightest etching by the fluoride, and weighing before and after use showed the loss from such etching, and therefore the contamination of the solution, to be negligible.

Spirit blue was used as an indicator, and gave very good results, except with potassium carbonate, which bleached it quickly. Phenol phthalein was later used with this salt, a few minute crystals of the solid being sufficient. The function of the indicator was to color the alcoholic upper layer, and render it easily visible when only a trace of it was present.

No attempt was made to work in a thermostat, or to control the temperature very closely, as it was found that in most cases a variation of two or three degrees produced a negligible change in the end-point, and if the results were to be used as a basis of an analytical method, it would be better to determine the curve under such temperature conditions as would be practical in its use. With propyl alcohol, where temperature was found to be more important than with the rest, the temperature was frequently taken with a calibrated thermometer, and kept as close as possible to that of the room (20 to 25° C.) The heat of dilution of the salts and alcohol, and that of the hands tended to keep the temperature a little higher than that of the laboratory, and where not otherwise stated, the temperature may be assumed to have been between 23 and 26° C. Care was taken to avoid loss by evaporation or other cause during a series, and whenever a thermometer was introduced, it was done just before a fairly large quantity of either alcohol or water was to be added, and the latter was used to wash off the bulb as the thermometer was withdrawn.

Specific Gravity Determinations. All specific gravity determinations were made with the pycnometer, weighing in a room whose temperature was within a degree or two of that of the alcohol. Two 50 cc. pycnometers were used. They were of the type which has a thermometer ground into one neck of the flask and a capillary tube in the other neck. The capillary was always filled to a definite mark, and covered with a cap when weighing. The alcohol was never allowed to expand enough during the weighing to reach the top of the capillary. Pycnometer No. 1, used in all determinations except those on methyl alcohol, was carefully standardized by repeated weighings empty and full of distilled and redistilled water at a temperature of 15.55° C. This temperature was used in all determinations with this pycnometer, except a few with propyl alcohol, q. v. Pycnometer No. 2 was similarly standardized at 4.00° C., for use with methyl alcohol, since the tables of Dittmar and Fawsett refer to water at that temperature. In all pycnometer determinations, great care was taken that the alcohol in the apparatus was kept thoroughly stirred, by frequently rotating the pycnometer rapidly about its axis. Since the room was at approximately the correct temperature, it was easy to control the temperature of the alcohol within 0.05° and fill the pycnometer exactly to the mark at the desired temperature. Duplicate determinations generally agreed within 0.00005. The thermometers in both instruments were graduated to 0.2° and could easily be read to 0.05°. They were standardized by comparison with a certified standard gradated to 0.02°.

Hehner's tables for ethyl alcohol and Dittmar and Fawsett's for methyl alcohol were used. For weak solutions of propyl alcohol the recent table of Doroshevskii and Rozhdestvenskii[1] was used, and for the strong alcohol a

[1] J. Russ. Phys. Chem. Soc., **41**, 1428; C. A., 1911, **5**, 409; Chem. Zentr., 1910, i, 812.

table constructed as explained later under propyl alcohol. For weak propyl alcohols, the determinations were made at 15.0/15.55°, and considered to be close enough to the conditions of Doroshevskii and Rozhdestvenskii (15./15°.).

MATERIALS

Methyl Alcohol. This was Kahlbaum's absolute methyl alcohol. Its specific gravity was taken at 15.55/4.00°, and three determinations gave 0.795762, 0.795875 and 0.795877. Dittmar and Fawsett give the specific gravity of absolute methyl alcohol at 15.55/4.00° as 0.79589. The agreement was considered satisfactory, and the alcohol was figured as 100 per cent pure in the calculations.

Ethyl Alcohol. Ordinary "95 per cent" alcohol was digested with silver nitrate and caustic potash to remove aldehydes, and then twice distilled. Ten litres of this were prepared and thoroughly mixed. It was preserved in large glass-stoppered bottles, from which portions of about 500 cc. were poured off into a smaller bottle for use as needed, thus preserving the main portion from possible contamination. The specific gravity of this alcohol was taken at 15.55/15.55°, and the following results obtained: 0.81923, 0.81920, 0.81916, 0.81919. From the average of the above determinations, it was found that the preparation contained 91.28 per cent by weight of absolute ethyl alcohol.

Propyl Alcohol. For the determination of the binodal curves Merck's normal propyl alcohol was used. It contained some water, and possibly some isopropyl alcohol. On distilling 100 cc. of it, 24 cc. came over between 91 and 94° C., and 63 cc. between 94 and 99°. Partial drying of this alcohol with anhydrous potassium fluoride seemed to increase the proportion of the upper fraction. It is well known that the presence of water lowers the boiling point of propyl alcohol, the constant-boiling mixture boiling below 90°. The specific gravity of this alcohol was taken at 20.0/15.55°, and the values found were 0.80812 and 0.80824. Some of the alcohol was treated with magnesium amalgam in excess, with which it reacted quite vigorously at first, and more slowly later. It stood with this for two weeks, with occasional shaking. Most of the action ceased within a few hours, but some slow action was noticeable for several days. The clear liquid was filtered into a distilling flask and distilled, care being taken to protect the distillate from the air. Distillation began at 95°, and practically all of the liquid distilled over below 99°. At 15.55/15.55° the distillate had a specific gravity of (1) 0.80644, (2) 0.80647, average 0.80646. The specific gravity of absolute propyl alcohol is given[1] as 0.8066 at 15° which is in good agreement

[1] Linnemann, Ann., **161**, 26.

with the above. Very recently Doroshevskii and Rozhdestvenskii[1] have found a higher value (.80804) but details of the purification of their material were not available to me. They appear to be the first ones to have worked out a complete table of specific gravities of the mixtures of normal propyl alcohol and water, but as their absolute alcohol was heavier than mine, I have used their table only for very dilute solutions. Using the absolute alcohol described above (71 gm.) in a glass-stoppered Erlenmeyer flask, I added successive amounts of distilled water, making duplicate determinations of the specific gravity of the diluted alcohol resulting from each addition. The amount of diluted alcohol remaining in the flask after each set of determinations was carefully weighed before adding fresh water, and the weight of absolute alcohol in it calculated afresh from its known strength, to correct for losses of the diluted alcohol. The following results were obtained:

TABLE 1

Alcohol, per cent by weight	Specific Gravity at 20.00/15.55°		
	(a)	(b)	Average
100.00	.80319	.80309	.80314
98.065	.80587	.80582	.80585
97.997	.80829	.80834	.80831
96.21	.81252	.81255	.81253
94.28	.81679	.81679	.81679
92.27	.82125	.82121	.82123
90.15	.82578	.82573	.82576
86.77	.83292	.83291	.83291

These results were plotted and formed a smooth curve. From this curve and the above results, the following table representing the per cent of normal propyl alcohol in distillates from Merck's propyl alcohol (which may be taken as perhaps typical of the best commercial alcohol) was constructed:

TABLE 2

Alcohol, per cent	Sp. G. at 20./15.55°	Alcohol, per cent	Sp. G. at 20./15.55°
100.00	.80314	92.00	.82185
99.00	.8058	91.00	.82395
98.00	.8083	90.00	.8261
97.00	.8108	89.00	.82825
96.00	.8130	88.00	.83035
95.00	.8153	87.00	.8325
94.00	.8175	86.00	.8346
93.00	.8197		

This table was used to determine the strength of all high-proof alcohol obtained in the following work. According to it, Merck's alcohol, which was used for most of this work, contained 98.07 per cent by weight of absolute alcohol.

[1] J. Russ. Phys. Chem. Soc., **41**, 1428; Chem. Zentr., 1910, i, 812. C. A., 1911, **5**, 409.

The quadruple-point determinations, and determinations of the solubility of salts in strong propyl alcohol were made with some of the above alcohol which had been once used in work on the binodal curves, salted out and recovered, and distilled in a fractionating apparatus. The alcoholic portions were dried with anhydrous potassium fluoride, and fractionated twice. The distillate from 90 to 97° had a specific gravity of .80986 (97.26 per cent), that from 97 to 98° .80418 (99.60 per cent), and that from 98 to 100° .80385 (99.73 per cent). The fraction boiling above 100° was rejected, and that from 90 to 97° set aside for further purification. The two fractions left (97 to 100°) were mixed and found to have a specific gravity of .80413 (99.63 per cent).

Potassium Fluoride. Merck's C. P. potassium fluoride was used, except in some preliminary experiments. The salt when freshly dissolved was neutral to phenol phthalein, but the solution quickly became slightly alkaline. Several grams of it dissolved in distilled water and acidified with nitric acid gave only a slight opalescence with silver nitrate. It was readily and completely soluble in water (except when the solution was nearly saturated, when cloudiness was noticed), and hence could have contained only a trace of fluosilicate. No appreciable amount of sodium could be shown by the spectroscope. 7.26 gm. of it, after fuming down with sulphuric acid, diluting and boiling with nitric acid, gave only 0.0002 gm. of material precipitated by ammonia and ammonium chloride. Tests for calcium and magnesium in the filtrate gave negative results. An attempt to remove the trace of fluosilicate present by treating with a little of Merck's best hydrofluoric acid, evaporation and ignition in platinum seemed rather to increase the amount of insoluble matter, so the salt was used as it was, after ignition for 5 to 10 minutes at moderate red heat, and cooling (covered) in a desiccator.

Potassium Carbonate. Merck's potassium carbonate "Highest Purity, Medicinal" was used. At first the solid salt was simply ignited and weighed, but some suspended matter was present and very troublesome, so a large amount of the salt was dissolved in a little more than its own weight of water, filtered by suction, and portions of this solution evaporated in platinum and heated to red heat as needed. The insoluble matter seemed to consist of iron compounds, with some lighter colored material. The solubility of the salt at room temperature was determined by evaporation and ignition of weighed quantities of the filtered saturated solution which had stood at least a week in contact with the hydrate. Duplicate determinations, two weeks apart, gave 53.05 and 53.07 per cent of the solution as anhydrous carbonate.

Sodium Chloride. Kahlbaum's sodium chloride "C. P. zur Analyse" was used, the crystals being ignited for several minutes and cooled in a desiccator before weighing. Its solubility was determined as in the case of the carbonate, duplicate determinations giving 26.35 and 26.31 per cent of the

solution as chloride, or 35.78 and 35.70 gm. salt dissolved in 100 gm. of water. Armstrong and Eyre[1] state that they find that the solubility at 25° varies somewhat in different samples. They found the values 35.71, 35.77, 35.83, 35.78, 36.08, and 36.19 gm. per 100 gm. water, while previously[2] they had found 36.14, 36.14, 36.22 and 36.23 gm. I have therefore taken the mean of my determinations as the solubility of my sample, and plotted it in the proper place. (See the system Propyl Alcohol, Water, Sodium Chloride.)

EQUILIBRIUM BETWEEN POTASSIUM FLUORIDE, ETHYL ALCOHOL AND WATER

This has never previously been studied. The literature on potassium fluoride, and the statements of those who may have noticed its salting-out power, have been given on page 6. Points on the binodal curve were determined at room temperature, according to the methods previously described, and are given in table 3. The effect of a change in temperature on the binodal curve is very small, apparently less than with potassium carbonate, and the results may be considered as being sufficiently accurate at any temperature between 23 and 26°. For determination of the concentration at the quadruple point where the two layers E and F (fig. 2) are in equilibrium with the solid hydrate $KF.2H_2O$ and their vapor, three separate determinations of the alcohol content of the upper layer were made. In an Erlenmeyer flask were placed a couple of hundred cubic centimeters of the aldehyde-free alcohol, water and quite a little potassium fluoride were added, the mixture warmed until all the hydrate formed was melted, shaken vigorously for some time, then cooled to room temperature with shaking. If the hydrate did not crystallize out in quite a large quantity, more of the anhydrous salt was added and the process repeated. When a sufficient amount of the crystalline hydrate appeared to be forming, the mixture was allowed to stand a week or more at room temperature, with frequent shaking, and then part of the upper liquid was cautiously poured off from the mixture of crystals and saturated solution, and carefully distilled to dryness. The specific gravities of the distillates obtained by three such experiments were 0.81283, 0.81221 and 0.81243, showing that the solvent in the upper layer at this point contained 93.63, 93.85, and 93.78, or an average of 93.75 per cent alcohol by weight, and 6.25 per cent water. Two portions of 20.14 and 10.43 gm. of these solutions gave respectively 0.2640 and 0.1193 gm. of potassium flouride, after evaporation in platinum and ignition. This indicates that at the quadruple point where we have two liquid phases, the upper one contains

[1]Proc. Roy. Soc., (A), **84**, 123. [2]Proc. Roy. Soc., (A), **79**, 566.

93.75 gm. alcohol, 6.25 gm. water, and 1.25 gm. of potassium fluoride per 100 gm. of solvent, or 92.69 per cent alcohol, 6.07 per cent water and 1.23 per cent potassium fluoride by weight.

An alcohol determination in the lower layer, decanted off from the crystals and separated from the upper layer, gave the following result: 166.86 gm. of the solution, to which some water had been added, were dis-

TABLE 3

Binodal Curve for the System: Water, Ethyl Alcohol, Potassium Fluoride. Determined at room temperature. 91.28% *alcohol used.*

Solvent added		Total weight present			Grams per 100 gm. solvent			Percent by weight		
Water	Alcohol	KF	H_2O	C_2H_5OH	KF	H_2O	C_2H_5OH	KF	H_2O	C_2H_5OH
50.833	34.382	11.658	53.832	31.383	13.680	63.17	36.83	12.03	55.57	32.40
4.627	8.935	11.658	59.238	39.539	11.802	59.97	40.03	10.56	53.64	35.80
3.428	7.628	11.658	63.331	46.502	10.614	57.66	42.34	9.60	52.13	38.28
6.368	19.234	11.658	71.376	64.059	8.608	52.70	47.30	7.93	48.52	43.55
3.781	17.448	11.658	76.678	79.986	7.441	48.94	51.06	6.93	45.55	47.52
8.578	36.201	11.658	88.412	113.031	5.787	43.89	56.11	5.47	41.49	53.04
6.700	34.047	11.658	98.080	144.110	4.813	40.50	59.50	4.59	38.64	56.77
6.284	39.059	11.658	107.770	179.763	4.054	37.48	62.52	3.90	36.02	60.08
5.290	36.963	11.658	116.283	213.503	3.535	35.26	64.74	3.41	34.06	62.53
6.383	60.504	11.658	127.941	268.732	2.939	32.25	67.75	2.86	31.33	65.81
33.613	.693	24.619	33.673	.633	71.762	98.15	1.85	41.78	57.14	1.08
5.662	.516	24.619	39.380	1.104	60.811	97.27	2.73	37.82	60.49	1.70
6.032	.672	24.619	45.471	1.717	53.387	96.36	3.64	34.81	62.82	2.37
5.316	.886	24.619	50.855	2.535	46.111	95.25	4.75	31.56	65.19	3.25
6.833	1.544	24.619	57.823	3.944	39.857	93.61	6.39	28.50	66.93	4.57
7.941	2.718	24.619	66.001	6.425	33.992	91.13	8.87	25.37	68.01	6.62
11.344	6.210	24.619	77.887	12.093	27.360	86.56	13.44	21.48	67.96	10.55
6.223	6.370	24.619	84.665	17.908	24.001	82.54	17.46	19.36	66.56	14.08
31.666	.416	26.623	31.702	.380	82.985	98.82	1.18	45.35	54.00	.65
18.266	1.811	26.623	50.126	2.033	51.042	96.10	3.90	33.79	63.63	2.58
11.720	2.323	26.623	62.049	4.153	40.215	93.73	6.27	28.68	66.85	4.47
9.093	3.417	26.623	71.441	7.272	33.823	90.76	9.24	25.27	67.82	6.91
15.137	9.786	26.623	87.430	16.205	25.688	84.36	15.64	20.44	67.12	12.44
6.511	6.778	26.623	94.532	22.392	22.770	80.85	19.15	18.55	65.85	15.60
11.391	18.162	26.623	107.507	38.970	18.176	73.40	26.60	15.38	62.11	22.51
7.068	15.851	26.623	115.957	53.439	15.717	68.45	31.55	13.58	59.15	27.27
10.633	26.255	26.623	128.879	77.405	12.906	62.48	37.52	11.43	55.34	33.23
5.404	14.772	26.623	135.571	90.889	11.756	59.87	40.13	10.52	53.57	35.91
25.390	22.357	5.039	27.339	20.408	10.554	57.26	42.74	9.55	51.79	38.66
2.819	9.152	5.039	30.956	28.762	8.439	51.84	48.16	7.78	47.81	44.41
3.397	12.333	5.039	35.428	40.020	6.679	46.96	53.04	6.26	44.02	49.72
2.226	10.871	5.039	38.602	49.943	5.691	43.60	56.40	5.39	41.25	53.36
3.728	20.921	5.039	44.154	69.040	4.452	39.01	60.99	4.26	37.35	58.39
3.149	20.849	5.039	49.121	88.071	3.673	35.80	64.20	3.54	34.53	61.93
3.021	27.001	5.039	54.496	112.718	3.014	32.59	67.41	2.93	31.64	65.44
*2.369	31.867	5.023	59.467	141.436	2.500	29.60	70.40	2.44	28.88	68.68
2.613	53.998	5.023	66.789	190.725	1.951	25.94	74.06	1.91	25.44	72.64
2.198	71.807	5.023	75.248	256.271	1.515	22.70	77.30	1.49	22.36	76.15
79.905	1.391	66.712	80.027	1.269	82.061	98.44	1.56	45.07	54.07	.86
7.348	.464	66.712	87.415	1.693	74.866	98.10	1.90	42.81	56.10	1.09
6.749	.472	66.712	94.205	2.124	69.254	97.80	2.20	40.92	57.78	1.28
.....	.....	.....	.....	.....	1.171	15.72	84.28	1.16	15.54	83.30

*Part of preceding solution lost in transferring to a new flask.

tilled for some time after the thermometer in the distilling flask had become stationary at 100°. Distilled water was added to the distillate, and the whole weighed 123.60 gm. This had a specific gravity of 0.99828 at 15.55/15°.55, and therefore contained 0.90 per cent by weight, or 1.11 gm. alcohol. This would give the lower solution an alcohol content of 0.67 per cent by weight, or 1.28 gm. per 100 gm. solvent.

The points on the binodal curve were determined as previously described, except the point at 84.28 per cent alcohol, which was determined by distillation of the alcohol from the upper one of two conjugate solutions, and

determination of the specific gravity of the distillate. The per cent of potassium fluoride was determined by evaporation of a weighed amount of this solution in a platinum dish, and ignition.

Two sets of conjugate solutions were taken, and the fluoride content of each determined, in order to locate tie-lines and get the approximate position of the plait-point. Since there was a loss of hydrofluoric acid possible during the evaporation of solutions containing such a large proportion of water, an excess of concentrated hydrochloric acid was added to each sample, after weighing it into the platinum dish, and the salt weighed as chloride after evaporation and cautious ignition. In the first determina-

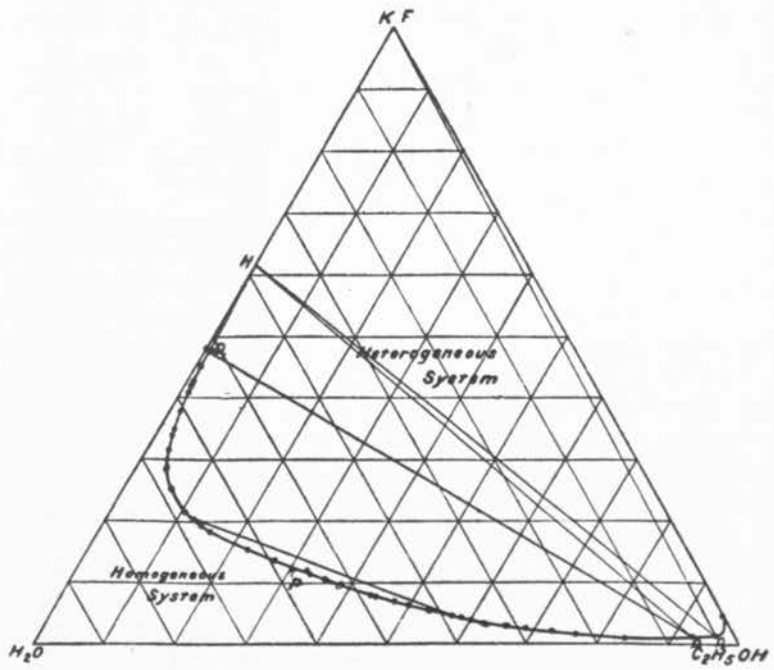

Figure 3. Equilibrium in the System: Potassium Fluoride, Ethyl Alcohol, Water.

tion 13.60 and 7.61 gm. of the upper and lower solutions respectively gave 0.7793 and 2.0435 gm. chloride, equivalent to 0.6073 and 1.5926 gm. fluoride. The two conjugate solutions then contained 4.47 and 20.9 per cent by weight of potassium fluoride, or 4.68 and 26.55 gm. per 100 gm. solvent. By reference to table 4, these solutions were found to contain 14.4 and 60.0 gm. alcohol per 100 gm. solvent, or 11.9 and 57.4 per cent by weight of alcohol. Similar determinations of another set of conjugate solutions showed them to contain 9.68 and 18.59 gm. potassium fluoride and 44.8 and 25.84 gm. alcohol per 100 gm. solvent, or 8.82 and 15.7 per cent potassium

fluoride and 41.0 and 21.8 per cent alcohol by weight. These two sets of conjugate solutions have been plotted, the tie-lines drawn, and plait-point indicated in figure 3.

A good many experiments were made to determine accurately the position of the second quadruple point, where the two solid phases (anhydrous salt and hydrate) were in equilibrium with a liquid and a vapor phase. Preliminary experiments showed that using ordinary commercial alcohol (about 92 per cent by weight) and the anhydrous fluoride, heating to boiling, cooling again to ordinary temperature and allowing to stand a short time to crystallize out excess of the hydrate gave about 96 per cent alcohol. In various other trials it was found easy to get from 96 to 96.5 per cent alcohol, but difficult to go above that amount by this method (heating and cooling). Some alcohol which had been treated several times in this way was heated with quite a little of the anhydrous salt in a pressure flask for several hours on a water bath, with no apparent change. It was then allowed to stand about eight months at room temperature, unopened. Upon filtering and carefully distilling to dryness, the alcohol had a specific gravity of 0.80196 at 15.55/15.55°, corresponding to 97.37 per cent by weight of alcohol. Some of the alcohol from previous treatments (96.13 per cent by weight) was refluxed with more fluoride, decanted off (hot) from the undissolved salt, allowed to stand until crystals of the hydrate formed, and then cooled to about —7° for an hour or two. After filtering through glass wool and distilling, the distillate was found to contain 96.85 per cent of alcohol, while a portion removed after only standing at room temperature contained 96.5 per cent. This process of refluxing and cooling to —5 or —7° was then repeated three times, and then upon distilling 97.3 per cent alcohol was obtained. The process of refluxing and cooling was then repeated six times, decanting into the same flask each time. The alcohol was then refluxed again, decanted back into the same flask, allowed to stand ten days at room temperature with this hydrate, decanted off, a weighed portion evaporated and ignited in platinum to determine the fluoride in solution, and the rest distilled to dryness for the alcohol determination. The distillate had a specific gravity of 0.80157 at 15.55/15.55°, and thus consisted of 97.50 per cent alcohol. 19.94 gm. of the solution gave 0.3025 gm. of potassium fluoride, which is 1.541 gm. per 100 gm. solvent or 1.52 per cent of the solution by weight.

A number of samples of alcohol of various strengths obtained from previous treatments, containing perhaps 96 per cent alcohol, were mixed and ground several days with some fluoride in an Abbé ball mill. The stones and the glaze of the mill were somewhat attacked. On decantation and distillation an alcohol having a sp. g. of 0.80172 (97.46 per cent by weight) was obtained. About 50 gm. of fluoride was added, and the mixture ground for five days more. A large amount of fluosilicate had now been formed,

and on decanting and distilling only 97.24 and 97.23 per cent alcohol was found in the distillate. 500 cc. of commercial alcohol was now ground about five days with 45 gm. of the anhydrous fluoride. After decantation and distillation an alcohol of sp. g. 0.80481 (96.43 per cent) was obtained. To this was then added the alcohol above mentioned (600-800 cc. 97.2 per cent) with about a liter of the alcohol (97.5 per cent) obtained by the boiling and freezing process, and about 240 gm. of fluoride. This was ground several days, and on distillation duplicate determinations showed the distillate to have a specific gravity of 0.80167 and 0.80155, showing 97.48 and 97.52 per cent by weight of alcohol.

From these determinations we may conclude that the alcohol which is in equilibrium with the mixture of the anhydrous fluoride and the hydrate contains 97.50 per cent alcohol and 2.50 per cent water, and that the solution of the salt under these conditions contains 1.52 per cent fluoride, 96.05 per cent alcohol and 2.43 per cent water by weight. This value has been plotted on the curves showing the equilibrium.

To determine the solubility of the fluoride in absolute alcohol, about 200 cc of Merck's absolute alcohol (sp. g. .79527, 99.58 per cent by weight) was treated in a stoppered flask with an excess of potassium fluoride which had been freshly ignited and quickly pulverized. The mixture was heated for some time at about its boiling point, with frequent shaking, and then allowed to stand for a couple of weeks at room temperature, with frequent shaking. 28.63 and 36.45 gm. of this solution gave on treatment with concentrated hydrochloric acid, evaporation and ignition, 1.6887 and 2.1416 gm. potassium chloride, equivalent to 1.3061 and 1.6690 gm. fluoride, or 4.56 and 4.58 per cent by weight of potassium fluoride (4.79 gm. per 100 gm. solvent.)

It is noticeable that although the fluoride is very soluble in water (the saturated solution containing 48 per cent of the anhydrous salt, or 92.3 gm. per 100 gm. water,[1] yet the addition of water to the solution in absolute alcohol decreases the solubility to a marked extent; from 4.79 gm. per 100 gm. solvent at practically 100 per cent alcohol, to 1.54 gm. per 100 gm. solvent in 97.5 per cent alcohol, and 1.17 gm. per 100 gm. solvent in 84 per cent alcohol. A similar decrease in solubility with the first increase in water content of the alcohol appears in the case of the fluoride with propyl alcohol, and the carbonate with all three alcohols, but not with sodium chloride and propyl alcohol. It is interesting to note that the solubility of the fluoride in absolute ethyl alcohol is approximately the same as in 60 per cent alcohol.

In general, the solubility of a salt in aqueous alcohol decreases as the concentration of the alcohol increases.[2] But L. de Bruyn has shown[3]

[1]Mylius and Funk, Ber., 1897, **30**, 1716.
[2]Gerardin, Ann. chim. phys., (4), **5**, 129.
[3]Z. phys. Chem., 1892, **10**, 782.

that in absolute methyl alcohol the hydrated salts $MgSO_4.7H_2O$, $ZnSO_4.7H_2O$, $CoSO_4.7H_2O$, $NiSO_4.7H_2O$, $FeSO_4.7H_2O$, $NiSO_4.6H_2O$, and $CuSO_4.5H_2O$, were readily soluble, but were quickly precipitated again as the lower hydrates (especially on adding a drop of water), or as lower hydrates in which part of the water of crystallization was replaced by alcohol. In 93 per cent alcohol they were only slightly soluble, and less so in the more dilute alcohols down to 50 per cent. He states that ethyl alcohol shows a similar behavior, but that it is less marked. Bödker[1] found that anhydrous cobalt and copper chlorides were very soluble in absolute alcohol, but that the addition of water caused the immediate precipitation of the hydrate. The results here shown with potassium carbonate and fluoride seem to be somewhat similar in principle, though of an entirely different class of salt, as far as the degree of hydration is concerned. But dilution of the solution of the anhydrous fluoride with water failed to produce precipitation of the hydrate, probably on account of supersaturation phenomena, which were frequently noticed with alcoholic solutions of the hydrate which had been prepared at high temperatures and cooled out of contact with the solid phase. It is particularly noticeable that sodium chloride, which does not form a crystalline hydrate at ordinary temperatures, was least soluble in the strongest propyl alcohol.

Beside the well-known methods for the determination of alcohol by the specific gravity of a solution, and by its boiling point (ebullioscope), many others have been studied in the attempt to find advantageous methods. Oxidation with either bichromate or permanganate has been tried by many.[2] The refractive index of mixtures of alcohol and water offers another method which has been well studied, and apppears to be of practical value in some cases.[3] Indirect methods, depending on the change in specific gravity of a liquor after removing alcohol by evaporation and making up again to the same volume, have been discussed by a number of authors.[4] The surface tension of the solution has been used to determine the alcoholic content,[5] as have also the lowering of the freezing point,[6] the solubility of cinchonine in

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[1]Z. phys. Chem., 1897, **22**, 505.

[2]Thresh, Chem. News, **38**, 251; Röse, Z., angew. Chem., **1**, 31; Bourcart, Bull. Soc. Ind. Mulhouse, **59**, 558, J. Chem. Soc., 1890, **58**, 1030; Frankland and Frew, J. Chem. Soc., 1891, **59**, 93; Grünhut, Chem. Zeit., **15**, 847, J. Chem. Soc., 1892, **62**, 1031; Benedikt and Neudörfer, Chem. Zeit., **16**, 77; Kuriloff, Ber., 1897, **30**, 741; Benedict and Norris, J. Am. Chem. Soc., 1898, **20**, 293; Lassar-Cohn, Z. anal. Chem., 1899, **38**, 251; Argenson, Bull. soc. chim., 1902, (3), **27**, 1000; Pozzi-Escot, Ann. chim. anal., 1902, **7**, 11; 1904, **9**, 126; Nicloux, Ann. chim. anal., 1904, **9**, 214; Martin, Rev. intern. Falsif., 1904, **17**, 48, J. Chem. Soc., 1904, **86**, ii, 520; Janak, Oesterr. Chem. Ztg., (2), **14**, 17, C. A., 1911, **5**, 2761.

[3]Riegler, Z. anal. Chem., 1896, **35**, 27; Ling and Pope, J. Fed. Inst. Brewing, 1901, **7**, 170, J. Chem. Soc., 1901, **80**, ii, 628; Leach and Lythgoe, J. Am. Chem. Soc., 1905, **27**, 964; Ackermann and Steinmann, Zeit. ges. Brauw., **20**, 259, Chem. Zentr., 1905, ii, 1672; Ackermann, Ann. chim. anal., 1905, **10**, 171; Kamenetzky, Chem. Ztg., **31**, 257; Doroschevskii and Dvorzhanchik, J. Russ. Phys. Chem. Soc., **40**, 101, **41**, 849, C. A., 1908, **2**, 2181, **4**, 135, 1403; Race, J. Soc. Chem. Ind., **27**, 547; Andrews, J. Am. Chem. Soc., 1908, **30**, 353; Frank-Kamenetsky, Z. angew. Chem., **23**, 293; Sidersky, Bull. assoc. sucr. dist., **27**, 1168, C. A., 1910, **4**, 2759, Ann. chim. anal., **16**, 142, C. A., 1911, **5**, 2143.

[4]Blunt, Analyst, 1891, 221; Richmond, J. Fed. Inst. Brewing, 1896, **2**, 529, J. Chem. Soc., 1897, **72**, 193; Leonard and Smith, Analyst, **22**, 225; Pharm. Zentr., **49**, 971; Günzel, Z. Nahr. Genussm., **18**, 206, C. A., 1909, **3**, 2717; Bonis, Ann. fals., **4**, 276, C. A., 1911, **5**, 3492.

[5]Duclaux, Ann. chim. phys., (5), **2**, 233; Gossart, Compt. rend., **113**, 537.

[6]Gaunt, Z. anal. Chem., 1905, **44**, 106.

chloroform containing alcohol,[1] the Pasteur drop reaction,[2] and the color produced by cobalt salts in the presence of a sulphocyanide.[3]

More closely allied to the method which I have to propose are the methods of Hager[4] and Böttger[5] who shake out the alcohol from essences with glycerine, and measure the increase of volume; Curtis,[6] who titrates alcohol of 85 per cent or over with toluene; and Bohlig,[7] who salts out the alcohol with potassium carbonate, and measures the volume of the layer obtained, standardizing the apparatus with known weights of absolute alcohol.

Methods involving the critical temperature of solution of alcohol-water mixtures with other liquids have also been worked out. The method of Crismer,[8] using kerosene, is said to be very accurate, but is only applicable to very strong alcohol, while the method of Buboux and Dutoit,[9] using a mixture of aniline and alcohol, is only suitable for mixtures containing from 8 to 12 per cent alcohol. An apparatus for the determination of alcohol, based on the solubility of ether in alcohols of various strengths (i. e., the binodal curve in the system alcohol, ether, water), has been patented and described.[10] As specially pure ether and 98 per cent alcohol are used to make the determination, it would hardly seem to be an easy and convenient method, and the accuracy may well be doubted.

If the binodal curve in the system containing a salt and aqueous alcohol has a small enough temperature coefficient, and can be determined with sufficient accuracy, it ought to be possible to add to a liquid of unknown alcoholic content enough of the salt to cause the solution to separate into two layers, and then, by the cautious addition of water, get the solution to be just homogeneous again. Now if the weights used are known, the composition of the original alcohol can be found, since the composition of the solution which we have made homogeneous is represented by that point on the binodal curve which expresses the relation of the amount of salt to the whole solution or to the amount of solvent present. Since, on the line separating the homogeneous from the heterogeneous system, there can only be one solution which contains this proportion of salt, this fixes the composition of the final solution definitely, and the weight of alcohol present can easily be computed.

While Schreinemaker's method for representing such equilibria, as described on a previous page, is convenient and useful in many ways, it is not suitable for determination of the slope of the curve for analytical purposes, as triangular coördinates are inconvenient and the most important

[1]Oudemans, Ann., **166**, 78, J. Chem. Soc., 1873, **26**, 533.
[2]Klöcker, Centr. Bakt. Parasitenk., II Abt., **31**, 108, C. A., 1912, **6**, 136.
[3]T. T. Monell, Chem. Zentr., 1877, 24. [4]Chem. Zentr., 1888, 1512.
[5]Chem. Zentr., 1872, 742. [6]J. Phys. Chem., 1898, **2**, 371. [7]Z. anal. Chem., **25**, 19.
[8]Bull. assoc. belge. des Chemistes, **16**, 83, Chem. Zentr., 1902, ii, 3.
[9]Ann. chim. anal., **13**, 4, see also Duperthuis and Philippe, Mitt. Lebensm. Hyg., **1**, 188, C. A., 1911, **5**, 3118.
[10]H. Kapeller, D. R. P., 213,127, Oesterr. ung. Z. Zuckerind. Landw., **38**, 817, C. A., 1910, **4**, 232, 2348; Sidersky, Ann. chim. anal. appl., **15**, 105, Bull. assoc. sucr. dist., **27**, 562, C. A., 1910, **4**, 1793, 1648.

part of the curve comes at a point where the figure is very much compressed. For this reason the results in table 3 have been calculated also on the basis of the weight of each component present in that quantity of the solution which contains 100 gm. of the solvent. Since the sum of the weights of water and alcohol here will be 100, this relation can be plotted in rectangular coördinates, the composition of the solvent being shown on one axis, and the amount of salt per 100 gm. solvent on the other. Such a curve also represents directly the solubility of the salt in alcohol of all strengths. In figure 4 such curves have been plotted for both potassium fluoride and potassium carbonate, and show well the difference between these salts in their behavior towards alcohol. It is noticeable that at concentrations above 30 grams of salt per 100 grams of solvent the curves are nearly identical, although above 50 grams per 100 gm. solvent, the solubility of the alcohol in the solution of the carbonate is a little less than that in the solution of the fluoride. It will be noted that the results for the fluoride form a smooth curve with which the individual results are in much better accord than is

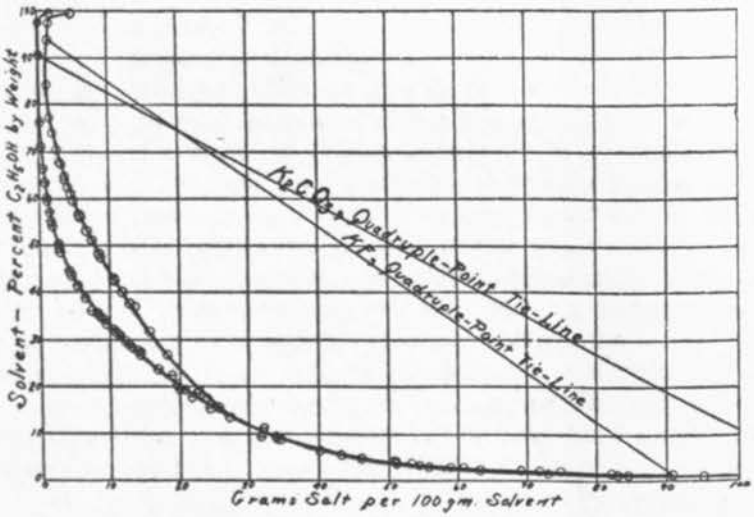

Figure 4. Equilibria in the Systems: Potassium Fluoride, Ethyl Alcohol, Water, and Potassium Carbonate, Ethyl Alcohol, Water.

the case with the carbonate. The end-point seemed to be more definite in the first case, and apparently the effect of temperature is less. For this reason the table recommended has been calculated on the basis of the fluoride curve, and is given in table 4.

To determine alcohol in an alcoholic liquid with this table, a stoppered flask is weighed, some freshly ignited potassium fluoride is weighed into it, a weighed amount of alcoholic liquid added, and the fluoride dissolved. From

the probable alcoholic content of the liquid used, the proportions of liquid and salt are so chosen that there will be salt enough to cause the liquid to separate into two phases; i. e., if a whiskey supposed to contain from 40 to 50 per cent alcohol is being tested, the salt should be in the proportion of at least 12 gm. per 100 gm. whiskey, and then a separation will take place, if the whiskey contains more than 39.4 per cent alcohol, as indicated by table 4. If the solution is now brought to approximately 25°, water added cautiously, with frequent shaking, until the solution just becomes homogeneous, and the whole weighed again, the proportion of the salt present to the total

TABLE 4

Determination of Alcohol by means of the Binodal Curve of the Ternary System: Water, Alcohol, Potassium Fluoride.

Gm. per 100 gm. solvent			Gm. per 100 gm. solvent		
KF	C_2H_5OH	d	KF	C_2H_5OH	d
60	2.82	.10	30	11.36	.72
59	2.92	.10	29	12.14	.78
58	3.02	.10	28	12.99	.85
57	3.13	.11	27	13.92	.93
56	3.24	.11	26	14.94	1.02
55	3.36	.12	25	16.07	1.13
54	3.48	.12	24	17.33	1.26
53	3.61	.13	23	18.75	1.42
52	3.75	.14	22	20.26	1.51
51	3.90	.15	21	21.80	1.54
50	4.06	.16	20	23.40	1.60
49	4.23	.17	19	25.10	1.70
48	4.41	.18	18	26.90	1.80
47	4.60	.19	17	28.8	1.9
46	4.80	.20	16	30.8	2.0
45	5.01	.21	15	32.9	2.1
44	5.24	.23	14	35.0	2.1
43	5.48	.24	13	37.2	2.2
42	5.74	.26	12	39.4	2.2
41	6.02	.28	11	41.7	2.3
40	6.32	.30	10	44.0	2.3
39	6.65	.33	9	46.4	2.4
38	7.01	.36	8	49.0	2.6
37	7.40	.39	7	51.9	2.9
36	7.83	.43	6	55.1	3.2
35	8.30	.47	5	58.7	3.6
34	8.81	.51	4	62.8	4.1
33	9.37	.56	3	67.5	4.7
32	9.98	.61	2	78.6	11.1
31	10.64	.66			

weight of solvent (whiskey plus water) gives, by reference to the table, the per cent of alcohol in such total weight of solvent, hence the weight of alcohol in the sample. For rapid work, if 100 gm. of the liquid under examination be taken, and all weights carried only to the nearest tenth of a gram, reasonably accurate results could be secured in a very few minutes. If extreme accuracy is not desired and care is taken in the preservation of the fluoride, it might be used without previous drying, making correction for water held as determined by one or two tests.

It is obvious that the method would not be very accurate in the presence of large quantities of dissolved solids, as in the case of a beer. But in the determination of alcohol in liquids where solids are absent, the good agreement of the data plotted in figure 4 with the smooth curve indicates that it would be satisfactorily accurate. One determination carried out on alcohol which had a sp. g. of 0.95233 (33.13 per cent by weight) gave 33.18 per cent. Heating the solution to 35° caused the solution to cloud a little, and when the titration was completed at that temperature 33.53 per cent of alcohol was found. The temperature coefficient for such a solution was evidently negligible within the range to which it would be easy to confine the temperature of the determination.

Since methyl alcohol is not precipitated by potassium fluoride, it was thought interesting to see what effect the presence of a certain amount of methyl alcohol would have on the determination of ethyl alcohol by this method. By weighing out some of the ethyl alcohol previously used, and mixing it with a weighed amount of absolute methyl alcohol, a solution was made containing 85.55 per cent ethyl alcohol, 6.27 per cent methyl alcohol, and 8.17 per cent water by weight. The weight of methyl alcohol was thus 7.33 per cent of the weight of absolute ethyl alcohol present. A series of determinations were made with this mixture and potassium fluoride, and

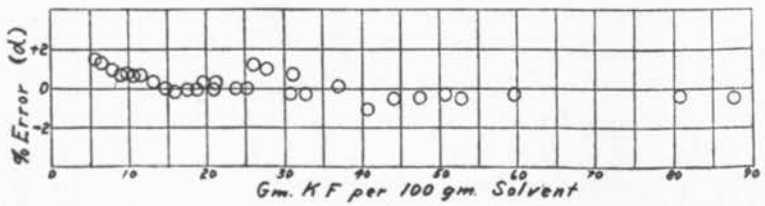

Figure 5. Determination of Ethyl Alcohol in the Presence of Methyl Alcohol.

the results are recorded in table 5, and plotted in figure 5. In plotting these, the quantity (d) chosen to be plotted against the concentration of the salt was the amount by which the per cent of ethyl alcohol in the solution was changed; i. e., the error in the determination of the ethyl alcohol caused by the presence of 7.33 per cent of its weight of methyl alcohol. A negative value indicates that too little alcohol would be found, on account of the increase in the solubility of the ethyl alcohol in the potassium fluoride solution, caused by the presence of the methyl alcohol, while a positive value indicates that too high a result would be found, the methyl alcohol here decreasing the solubility of the ethyl alcohol. It is surprising to note that in concentrated solutions there appears first a negative effect, over a wide range, and the methyl alcohol in the mixture acts as a solvent for the ethyl

alcohol, then conditions appear to be reversed, although the results are not very concordant. Then between 25 and 15 gms. salt per 100 gm. solvent, the determination is correct, within the limits of the experimental error, and from this point down, the solubility of the ethyl alcohol is decreased by the methyl alcohol to a constantly increasing extent. This is a phenomenon worthy of a further investigation, but it appears probable that within certain concentrations, ethyl alcohol can be satisfactorily determined in the presence of methyl alcohol by this method.

TABLE 5

Determination of Ethyl Alcohol in the presence of Methyl Alcohol by its solubility in solutions of Potassium Fluoride. Room temperature. Mixture used contains 85.55 *per cent* C_2H_5OH, 6.27 *per cent* CH_3OH *and* 8.17 *per cent* H_2O *by weight.*

Solvent added		Total weight present				Grams per 100 grams solvent				Correct	
Water	Mixture	KF	H_2O	C_2H_5OH	CH_3OH	KF	H_2O	C_2H_5OH	CH_3OH	C_2H_5OH	d
17.294	.380	15.500	17.325	.325	.024	87.699	98.02	1.84	.14	1.35	—.5
13.361	1.500	15.500	30.809	1.608	.118	47.641	94.70	4.94	.36	4.48	—.46
7.363	1.862	15.500	38.324	3.201	.235	37.117	91.77	7.67	.56	7.78	.11
11.849	5.667	15.500	50.636	8.049	.591	26.149	85.42	13.58	1.00	14.79	1.21
14.083	31.091	15.500	67.260	34.648	2.542	14.840	64.39	33.17	2.43	33.24	.07
10.618	31.370	15.500	80.442	61.486	4.510	10.585	54.93	41.99	3.08	42.65	.66
13.031	.291	10.776	13.055	.249	.018	80.889	98.00	1.87	.14	1.50	—.37
4.350	.359	10.776	17.434	.556	.041	59.764	96.69	3.08	.23	2.84	—.24
2.765	.391	10.776	20.231	.891	.066	50.861	95.49	4.21	.31	3.93	—.28
4.078	1.185	10.776	24.406	1.905	.140	40.741	92.27	7.20	.53	6.10	—1.10
6.315	1.788	10.776	30.867	3.435	.252	31.187	89.33	9.94	.73	10.51	.73
2.682	1.464	10.776	33.669	4.688	.344	27.846	87.00	12.11	.89	13.12	1.01
1.482	2.351	10.776	35.343	6.699	.491	25.336	83.10	15.75	1.15	15.70	.05
3.480	5.145	10.776	39.244	11.101	.814	21.065	76.71	21.70	1.59	21.70	.0
1.955	3.894	10.776	41.517	14.433	1.058	18.903	72.83	25.32	1.86	25.28	—.04
2.771	7.428	10.776	44.895	20.788	1.524	16.035	66.80	30.93	2.27	30.73	—.2
27.377	1.390	15.172	27.491	1.189	.087	52.741	95.56	4.13	.30	3.65	—.48
4.738	.919	15.172	32.304	1.975	.145	44.074	93.84	5.74	.42	5.22	—.52
8.850	2.972	15.172	41.397	4.518	.331	32.807	89.51	9.77	.72	9.49	—.28
1.941	1.108	15.172	43.428	5.466	.401	30.778	88.10	11.09	.81	10.84	—.25
7.695	6.650	15.172	51.667	11.155	.818	23.840	81.19	17.53	1.28	17.56	.03
3.086	4.317	15.172	55.106	14.848	1.089	21.356	77.57	20.90	1.53	21.25	.35
*2.065	3.891	15.172	57.476	18.174	1.333	19.708	74.66	23.61	1.73	23.90	.29
2.453	6.597	15.172	60.468	23.818	1.747	17.635	70.29	27.68	2.03	27.6	—.08
7.407	19.765	15.172	69.490	40.728	2.987	13.402	61.38	35.98	2.64	36.32	.34
4.166	12.372	15.172	74.667	51.313	3.763	11.694	57.55	39.55	2.90	40.1	.65
4.624	15.500	15.172	80.558	64.574	4.735	10.124	53.75	43.09	3.16	43.81	.72
4.445	15.972	15.172	86.308	78.239	5.737	8.910	50.68	45.95	3.37	46.63	.68
11.638	46.822	15.172	101.773	118.297	8.675	6.633	44.49	51.72	3.79	53.07	1.35
‡.....	.....	11.001	57.089	43.641	3.201	10.585	54.93	41.99	3.08	.....	.....
7.538	27.354	11.001	66.863	67.043	4.917	7.924	48.16	48.29	3.54	49.22	.93
9.254	44.872	11.001	79.784	105.432	7.732	5.702	41.35	54.64	4.01	56.17	1.53

*Lost .016 gm. on standing after the previous determination.
‡Part of the solution from the sixth determination.

SYSTEM POTASSIUM CARBONATE, ETHYL ALCOHOL, WATER

Potassium carbonate is a salt which is more often found in the laboratory than the fluoride, and therefore more convenient for analytical purposes, so this system was studied and the position of the binodal curve determined. This salt was the first ever noted as having the power to salt out alcohol, as it is known that Raymond Lully (1235-1315) used and described it for that purpose. The composition of the solutions formed was first studied by

Lescoeur,[1] who determined the composition of the upper layer at the quadruple point. He believed it to be a definite hydrate of alcohol, but he was evidently in error here, as shown by Schreinemakers.[2] A few determinations of points on the binodal curve were made by Linebarger,[3] but the points found all lie within a very narrow range (0.4 to 2.1 gm. carbonate per 100 gm. solvent) and the method used could not give very accurate results, as shown later, in the system: potassium carbonate, water, methyl alcohol.

B. de Bruyn[4] determined the concentration of the solutions in equilibrium at the quadruple point, at different temperatures. He says of the results, "The salt content of both layers increases with the temperature, the alcohol content changes less than the error of analysis. At 35° I found for alcohol in the upper layer 91.7, 89.8, 90.4, 91.6 per cent, in the table I have used the average. Lescoeur found 90.0 per cent twice, and 93.5 per cent, his figures vary among themselves more than mine, but the average agrees with the results in the table." His determinations nearest room temperature are at 17° and 35°. His alcohol determinations, according to his own statements, leave much to be desired. Bell[5] determined the composition of nine solutions lying on the binodal curve, and recently Cuno[6] determined the composition of eight sets of conjugate solutions. He states[7] that his results agree fairly well with those of Bell, although plotting them together shows that his curve lies above that of Bell for its whole length, the difference in alcohol content between solutions of the same salt content in the two curves being often nearly a percent. His results are the most complete which have been previously published, but his method of alcohol determination (by the conductivity of the solution) might be open to question, as a foundation for an analytical method. He says he did not determine the composition of the solutions at the quadruple point, on account of the difficulty of determining alcohol in such strong and such weak solutions.

As previously stated, some difficulty was experienced at times in getting good end-points with this salt, so a larger number of determinations were made than in the case of the fluoride. The figures will be found in table 6, and the complete curve in figure 6. This is the first time the complete figure for this system has been shown. The hydrate of the salt has been a matter of much dispute,[8] but the work of Foote and Sholes on the dehydration of alcohol and that of de Forcrand[9] show that the hydrate which is stable at ordinary temperature is $2K_2CO_3.3H_2O$. This has been introduced in the proper place in the diagram, which corresponds to the general one

[1] Bull. soc. chim., 1897, (3), **17**, 18.
[2] Z. phys. Chem. 1897, **23**, 649.
[3] Am. Chem. J., 1892, **14**, 380.
[4] Z. phys. Chem., 1900, **32**, 63.
[5] J. Phys. Chem., **9**, 531.
[6] Ber. physik. Ges., **5**, 735, Ann. Physik., **25**, 346.
[7] Ann. Physik., **28**, 663.
[8] For discussion of the earlier work see B. de Bruyn, loc. cit.
[9] Compt. rend., **148**, 1731.

previously described, although the line joining the saturated solution to the lower solution at the quadruple point (DE, fig. 2) is very short, and the triangle HDE is so small as to be invisible in the figure.

A number of tie-lines were located in an attempt to find the approximate location of the plait-point. They were determined by evaporation of weighed portions of conjugate pairs of solutions, ignition and weighing of the carbonate. By reference to table 6 it was easy to get the corresponding

TABLE 6

Binodal Curve for the System: Water, Alcohol, Potassium Carbonate, at room temperature. Alcohol used 91.28 *per cent by weight.*

Solvent added		Total weight present			Grams per 100 gm. solvent			Per cent by weight		
Water	Alcohol	K_2CO_3	H_2O	C_2H_5OH	K_2CO_3	H_2O	C_2H_5OH	K_2CO_3	H_2O	C_2H_5OH
26.678	1.228	14.122	26.785	1.121	50.606	95.98	4.02	33.60	63.73	2.67
12.015	4.169	14.122	39.164	4.926	32.030	88.83	11.17	24.26	67.28	8.46
11.518	7.354	14.122	51.323	11.639	22.429	81.51	18.49	18.32	66.58	15.10
6.209	5.429	14.122	58.005	16.595	18.930	77.75	22.25	15.92	65.37	18.71
12.516	11.011	14.122	71.481	26.646	14.392	72.85	27.15	12.58	63.68	23.74
14.296	13.053	14.122	86.915	38.561	11.255	69.27	30.73	10.12	62.26	27.62
11.501	11.788	14.122	99.444	49.321	9.493	66.85	33.15	8.67	61.05	30.28
22.042	22.585	14.122	123.455	69.937	7.302	63.84	36.16	6.81	59.50	33.70
31.754	14.190	6.056	32.991	12.953	13.181	71.81	28.19	11.65	63.45	24.91
4.362	4.460	6.056	37.742	17.024	11.058	68.92	31.08	9.96	62.06	27.98
8.337	9.176	6.056	46.879	25.400	8.379	64.86	35.14	7.73	59.85	32.42
9.258	11.840	6.056	67.169	36.208	6.486	61.22	38.78	6.09	57.49	36.42
8.724	12.149	6.056	66.952	47.298	5.301	58.60	41.40	5.03	55.65	39.32
9.047	13.743	6.056	77.197	59.843	4.419	56.33	43.67	4.23	53.95	41.82
9.825	16.184	6.056	88.433	74.616	3.714	54.24	45.76	3.58	52.30	44.12
16.081	28.920	6.056	107.036	101.014	2.911	51.45	48.55	2.83	49.99	47.18
33.375	.342	32.096	33.405	.312	95.192	99.07	.93	48.77	50.76	.48
9.873	.379	32.096	43.311	.658	72.997	98.50	1.50	42.20	56.94	.87
6.279	.488	32.096	49.633	1.103	63.261	97.83	2.17	38.75	59.92	1.33
6.195	.621	32.096	55.882	1.670	55.769	97.10	2.90	35.80	62.34	1.86
4.599	.598	32.096	60.533	2.216	51.150	96.47	3.53	33.84	63.82	2.34
5.058	.902	32.096	65.670	3.039	46.713	95.58	4.42	31.84	65.15	3.01
4.438	1.028	32.096	70.198	3.977	43.271	94.64	5.36	30.20	66.06	3.74
14.260	4.461	32.096	84.847	8.049	34.55	91.34	8.66	25.68	67.89	6.44
9.880	4.700	32.096	95.137	12.339	29.863	88.52	11.48	23.00	68.16	8.84
15.248	8.438	32.096	111.121	20.041	24.470	84.72	15.28	19.66	68.06	12.28
12.939	10.674	32.096	124.991	29.784	20.737	80.76	19.24	17.18	66.89	15.94
4.685	4.037	32.096	130.028	33.469	19.631	79.53	20.47	16.41	66.48	17.11
13.610	12.281	32.096	144.709	44.679	16.947	76.41	23.59	14.49	65.34	20.17
21.024	19.420	32.096	167.426	62.406	13.965	77.85	27.15	12.25	63.92	23.82
17.810	18.154	32.096	186.819	78.977	12.075	70.29	29.71	10.77	62.72	26.51
16.253	16.671	32.096	204.526	94.194	10.745	68.47	31.53	9.70	61.83	28.47
32.504	36.227	32.096	240.189	127.262	8.735	65.37	34.63	8.03	60.12	31.85
80.979	9.210	28.614	81.782	8.407	31.727	90.68	9.32	24.09	68.84	7.07
24.900	16.284	28.614	108.102	23.271	21.781	82.29	17.71	17.89	67.57	14.54
6.513	4.720	28.614	115.027	27.579	20.065	80.66	19.34	16.71	67.18	16.11
13.092	13.194	28.614	129.270	39.622	16.942	76.54	23.46	14.49	65.45	20.06
15.473	14.561	28.614	146.013	32.913	14.384	73.40	26.60	12.58	64.18	23.35
13.313	13.620	28.614	160.514	65.345	12.669	71.07	28.93	11.24	63.08	25.68
12.299	12.505	28.614	173.903	76.760	11.415	69.38	30.62	10.25	62.27	27.48
11.657	12.279	28.614	186.631	87.968	10.420	67.96	32.04	9.44	61.55	29.01
*19.167	21.809	28.614	207.680	107.866	9.068	65.82	34.18	8.31	60.35	31.34
17.522	19.392	28.614	226.893	125.567	8.118	64.37	35.63	7.51	59.63	32.96
(Distillation)		3.2511	.....	.....	1.635	44.86	55.14	1.61	44.14	54.25
18.230	17.294	1.482	19.738	15.786	4.172	55.56	44.44	4.00	53.33	42.66
6.755	13.486	1.482	27.669	28.096	2.658	49.62	50.38	2.58	48.34	49.08
7.026	15.714	1.482	36.065	42.440	1.888	45.94	54.06	1.85	45.09	53.06
6.487	17.075	1.482	44.041	58.026	1.452	43.15	56.85	1.43	42.53	56.04
#10.642	31.460	1.482	57.410	86.721	1.028	39.83	60.17	1.02	39.42	59.56
15.105	51.219	1.482	76.981	133.474	.704	36.58	63.42	.70	36.32	62.98
12.959	24.290	.393	15.077	22.172	1.055	40.48	59.52	1.04	40.06	58.90
3.745	13.760	.393	20.022	34.732	.718	36.57	63.43	.71	36.31	62.98
4.547	18.282	.393	26.163	51.420	.507	33.72	66.28	.50	33.55	65.95
6.497	41.333	.393	36.264	89.149	.313	28.92	71.08	.31	28.83	70.86
5.230	57.624	.393	46.519	141.748	.209	24.71	75.29	.21	24.66	75.13
2.553	29.489	.393	51.643	168.666	.178	23.44	76.56	.18	23.40	76.42
†84.488	.417	93.260	84.488	.417	109.840	99.51	.49	52.34	47.42	.23
†24.584	.931	93.260	109.072	1.348	84.459	98.78	1.22	45.79	53.55	.66
44.523	3.159	93.260	153.870	4.232	58.987	97.32	2.68	37.10	61.21	1.69

*Loss on standing 0.29 gm.
#Loss on standing 0.38 gm.
†Absolute alcohol was used in these two determinations.

per cents of alcohol and water. The following concentrations of potassium carbonate (in percent of the total weight of the solution) were found to exist in conjugate solutions: 0.241 and 39.11, 1.72 and 29.62, 4.03 and 25.7, 6.30 and 21.08, 8.29 and 19.15, 10.35 and 18.18. As previously noticed, the tie-lines are, in the triangular system, the straight lines joining the points representing the conjugate solutions. By calculation from the composition of two known conjugate solutions, it is easy to determine the composition of a mixture which will separate into given volumes of each of the two solutions. Such a calculation for the second set of conjugate solutions above recorded is plotted with the binodal curve in rectangular coördinates in figure 4. The computations were for the volume relations 1:1, 2:1, and 1:2, and as will be seen, they lie on the straight line joining the two conjugate solutions.

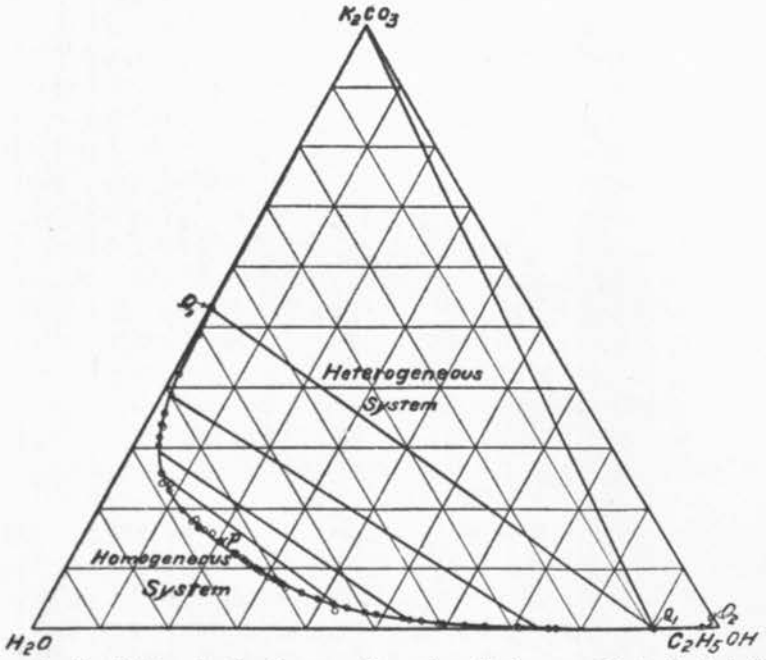

Figure 6. Equilibrium in the System: Potassium Carbonate, Ethyl Alcohol, Water.

Thus the tie-lines are straight lines in this system of representation also.

Two determinations of the alcoholic content of the upper solution at the quadruple point (Q_1, figure 6) were made by allowing a mixture of alcohol, strong carbonate solution, and the hydrate to stand several weeks, with repeated shaking, and then pouring off the upper layer, distilling to dryness, and determining the specific gravity of the distillate. Two different solutions thus prepared gave distillates with specific gravities of 0.82104 and 0.82093 at 15.55/15.55°, indicating that they contained respectively 90.63

and 90.67 per cent alcohol. Three determinations of the carbonate content gave 0.0953, 0.0869 and 0.1022 gm. per 100 gm. solvent, giving an average composition for the upper layer of alcohol 90.65, water 9.35 and potassium carbonate 0.095 gm. per 100 gm. solvent, or 90.56, 9.34, and 0.09 per cent by weight respectively. The average of the results of de Bruyn at 17° is 91.5 per cent alcohol and 0.06 per cent carbonate, and at 35°, 90.9 per cent alcohol and 0.07 per cent carbonate. Since his alcohol determinations at 35° ranged from 89.8 to 91.7 per cent, and those at 17° were presumably not more accurate, the agreement is as close as could be expected. For the lower layer, duplicate determinations gave 53.30 and 52.88 per cent carbonate and 0.273 and 0.283 per cent alcohol. The alcohol determination was made on 600 to 800 gms. of the solution, it being easy to get off all the alcohol in the first 50 cc. of the distillate, as shown by the boiling point of the solution, and in this the alcohol is easily determined. B. de Bruyn[1] found at 35°, 53.4 per cent carbonate and 0.2 per cent alcohol, at 17° 52.1 per cent carbonate and 0.2 per cent alcohol. It will be noted that the alcohol has not reduced the solubility of the salt appreciably, as the saturated aqueous solution contained 53.06 per cent carbonate. With methyl alcohol, which is more soluble in the strong carbonate solution, the solubility is markedly decreased.

The solubility of the salt in 97.5 per cent and in absolute alcohol, was determined as in the case of the fluoride, and saturated solutions at room temperature were found to contain (a) 0.0524 (b) 0.0564 and (a) 1.62 (b) 1.64 per cent of carbonate respectively, or an average of 0.054 per cent for 97.5 per cent alcohol and 1.63 per cent for 99.6 per cent alcohol. The same incease in solubility in the anhydrous alcohol is here to be noticed, as in the case of the fluoride. As the mixture of the anhydrous salt and the hydrate is in equilibrium with 99.6 per cent alcohol,[2] this is the other quadruple point, Q_2.

In table 7 will be found the approximate values of the solubility of ethyl alcohol, corrected from the curve in figure 4, over the range in which the curve is quite definitely determined. These values may be used for the determination of alcohol in the same manner as those in table 4, using potassium carbonate which has been ignited, and is free from insoluble impurities, but the use of the fluoride appears to give more accurate results.

In figure 4 the curves for both the fluoride and the carbonate are plotted, and the two quadruple-point tie-lines drawn. The determinations marked with a circle having a diameter drawn in are in the carbonate system, and it will be noticed that a number of them lie quite a distance from the line. The cause was the uncertainty in the end-point, due to suspended matter which obscures the disappearance of the emulsion. If the carbonate is to

[1] loc. cit.
[2] Foote and Sholes, loc. cit.

be used for the analytical method, it should be freed from such matter by solution in its own weight of water, filtration and evaporation. All weights given in the above and other tables refer to the anhydrous salt. Where a large number of determinations were to be made, a standard solution, containing 50 per cent of the anhydrous salt by weight, could easily be used, and allowance made for its water content. A crystal of solid phenol-phthalein is the best indicator.

TABLE 7

Gm. per 100 gm. solvent			Gm. per 100 gm. solvent		
K_2CO_3	C_2H_5OH	d	K_2CO_3	C_2H_5OH	d
45	5.0	.2	21	18.9	1.1
44	5.2	.2	20	20.0	1.1
43	5.4	.2	19	21.1	1.1
42	5.7	.3	18	22.3	1.2
41	6.0	.3	17	23.5	1.2
40	6.3	.3	16	24.7	1.2
39	6.6	.3	15	26.0	1.3
38	7.0	.4	14	27.2	1.2
37	7.4	.4	13	28.5	1.3
36	7.8	.4	12	29.8	1.3
35	8.3	.5	11	31.1	1.3
34	8.8	.5	10	32.5	1.4
33	9.3	.5	9	34.0	1.5
32	9.9	.6	8	35.7	1.7
31	10.5	.6	7	37.5	1.8
30	11.2	.7	6	39.6	2.1
29	11.8	.6	5	42.0	2.4
28	12.5	.7	4	44.7	2.7
27	13.2	.7	3	48.3	3.6
26	14.0	.8	2.5	50.3	2.0
25	14.9	.9	2	52.6	2.6
24	15.8	.9			
23	16.8	1.0			
22	17.8	1.0			

The curve and the table above given may be considered approximately correct for room temperature (23 to 26°). The effect of change of temperature was studied a little, and will be discussed under a later head (Temperature Coefficients and Critical Solution Temperatures).

SYSTEM POTASSIUM CARBONATE, METHYL ALCOHOL, WATER

This system was first investigated by Linebarger,[1] who made three determinations of points on the binodal curve. As shown in figure 7, his results are evidently far from accurate, as they lie on a curve which must be true for temperatures near zero. De Bruyn[2] determined the position of the

[1] Am. Chem. J., 1892, **14**, 380.
[2] Z. phys. Chem., 1900, **32**, 63.

quadruple point at 17 and 35°, three other tie-lines on the binodal curve at the first temperature and two at the second. He recalculated Linebarger's results and showed their inaccuracy, and gave a general ("schematisch") curve to show the form of the isotherm. This is reproduced in figure 8, to compare with the diagram of the isotherm which I have determined at room temperature (fig. 9) and the plot of the actual results obtained by him and by Linebarger (fig. 7). The only other work which appears to have been done on this system is that of Wrewsky,[1] who showed that the vapor pres-

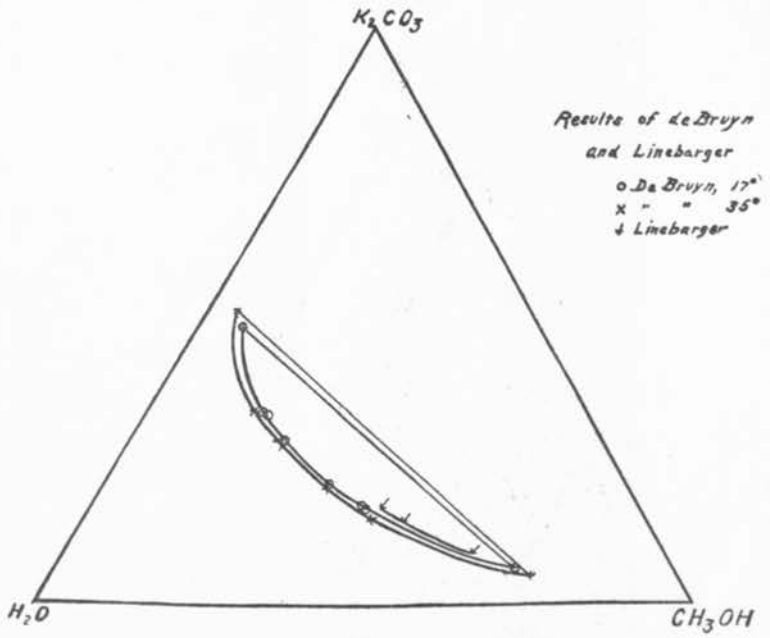

Figure 7. Plot of results of B. de Bruyn and Linebarger, in the System: Potassium Carbonate, Methyl Alcohol, Water.

sure of the system increased with the proportion of the salt present. He showed that, as was to be expected, the two layers formed in the system had the same vapor pressure, the partial pressure of the water being lowered and that of the alcohol raised by the presence of the salt. He also studied the effect of temperature on the vapor pressure of the system.

As potassium carbonate appears to be the only salt which is capable of precipitating methyl alcohol at ordinary temperatures, this system was studied to see how closely it resembled the others. The binodal curve was determined, as in the other cases, and the data are found in table 8. Deter-

[1] J. Russ. Phys. Chem. Soc., 1900, **32**, 593, J. Chem. Soc., 1901, **80**, ii, 56.

minations of the composition of the two layers in equilibrium at the quadruple point were made by the same methods as in the other cases. The upper solution was found to contain 76.22 and 75.48 per cent of methyl alcohol and 6.38, 6.22, and 6.36 per cent potassium carbonate, or an average of 75.85 per cent methyl alcohol and 6.32 per cent carbonate. Much trouble was experienced in distilling this solution, on account of the very violent bumping which took place, and the distillate had to be redistilled once or twice to get rid of all carbonate. The determinations on the lower solution showed 6.10 per cent of methyl alcohol and 49.01 and 49.09 per cent of carbonate.

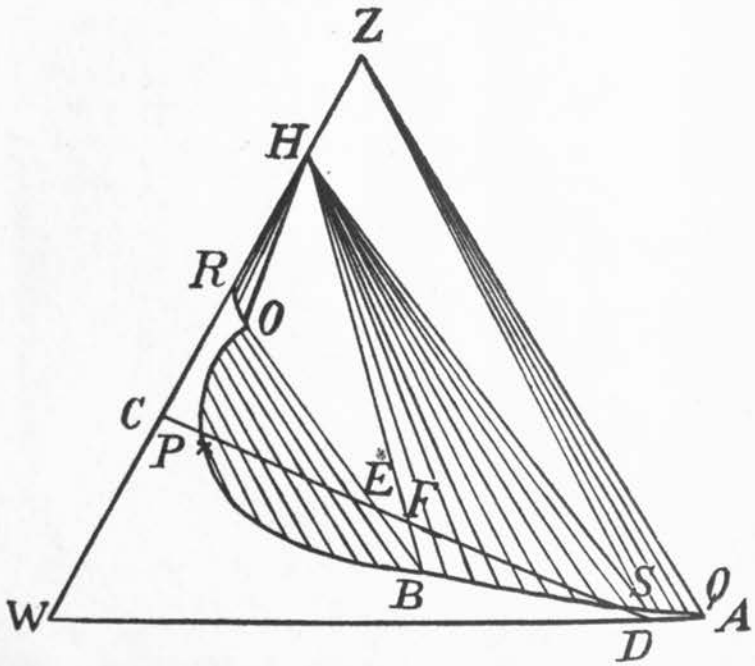

Figure 8. B. de Bruyn's Diagram for the System: Potassium Carbonate, Methyl Alcohol, Water.

A number of determinations of the solubility of the carbonate in stronger alcohol were made by weighing out quantities of the absolute alcohol and water to make a solution of known composition, adding a slight excess of the finely powdered anhydrous salt, shaking, sometimes warming, and allowing to stand for some weeks at room temperature, with frequent shaking. If the excess of carbonate appeared to be becoming less than a gram, more was added. From 80 to 160 gm. of the solvent were used in each case. With stronger alcohol, the time required to reach equilibrium was longer. Thus

using alcohol of 86.7, 90.5 and 96.5 per cent by weight, determinations after three weeks gave potassium carbonate 2.03, 1.38, and 1.84 per cent by weight of the respective solutions, while after five weeks the same solutions gave 2.05, 1.56 and 2.13 per cent by weight. The higher figure was accepted in the first two cases as approximately correct, and another solution made up for the latter. This solution, using 96.2 per cent alcohol, was digested for several hours at 40-50°, and after standing two weeks, with frequent shaking and occasional warming, showed in two duplicate determinations 2.72 and

TABLE 8

Binodal Curve for the System: Water, Methyl Alcohol, Potassium Carbonate, at room temperature. Absolute methyl alcohol used.

Solvent added		Total weight present			Grams per 100 gm. solvent			Per cent by weight		
Water	CH_3OH	K_2CO_3	H_2O	CH_3OH	K_2CO_3	H_2O	CH_3OH	K_2CO_3	H_2O	CH_3OH
45.997	8.504	37.327	45.997	8.504	68.489	84.40	15.60	40.65	50.09	9.26
11.425	12.757	37.327	57.422	21.261	47.440	72.98	27.02	32.18	49.50	18.33
5.935	10.210	37.327	63.357	31.471	39.363	66.81	33.19	28.25	47.94	23.82
14.308	26.276	37.327	77.665	57.747	27.566	57.35	42.65	21.61	44.96	33.43
8.020	16.879	37.327	85.685	74.626	23.284	53.45	46.55	18.89	43.36	37.76
8.895	19.944	37.327	94.580	94.570	19.734	50.00	50.00	16.48	41.76	41.76
9.764	23.979	37.327	104.344	118.549	16.747	46.81	53.19	14.34	40.10	45.56
13.487	36.455	37.327	117.831	155.004	13.681	43.19	56.81	12.03	37.99	49.97
11.839	38.198	37.327	129.670	193.202	11.561	40.16	59.84	10.17	35.33	52.64
5.917	26.851	37.327	135.587	220.053	10.496	38.12	61.88	9.23	33.53	54.43
24.008	3.404	21.496	24.008	3.404	78.418	87.58	12.42	43.95	49.09	6.96
8.311	7.871	21.496	32.519	11.275	49.084	74.25	25.75	32.92	49.80	17.27
9.964	17.844	21.496	42.483	29.119	30.122	59.33	40.67	23.15	45.60	31.26
7.905	16.257	21.496	50.388	45.376	22.447	52.62	47.38	18.33	42.97	38.69
10.019	23.678	21.496	60.407	69.054	16.604	46.66	53.34	14.24	40.02	45.74
4.531	12.922	21.496	64.938	81.976	14.632	44.20	55.80	12.55	37.91	47.85
7.578	22.652	21.496	72.516	104.628	12.135	40.94	59.06	10.82	36.51	52.67
14.550	53.276	21.496	87.066	157.904	8.775	35.54	64.46	8.07	32.67	59.26
6.228	38.591	21.496	93.294	196.495	7.418	32.19	67.81	6.91	29.97	63.13
*85.754	1.860	92.611	85.754	1.860	105.703	97.88	2.12	51.39	47.58	1.03
* 1.548	2.229	92.611	87.302	4.089	101.335	95.53	4.47	50.33	47.45	2.22
8.939	8.877	92.611	96.241	12.966	84.803	88.13	11.87	45.89	47.69	6.42
50.596	49.054	92.611	146.837	62.020	44.341	70.31	29.69	30.72	48.71	20.57
(Part of	above)	57.907	91.815	38.778	44.341	70.31	29.69	30.72	48.71	20.57
6.255	11.340	57.907	98.070	50.118	39.077	66.18	33.82	28.10	47.59	24.32

*These two points are not on the binodal curve, but are on the curve of saturated carbonate solutions not saturated with alcohol.

2.72 per cent by weight. A sample of the absolute alcohol, similarly treated, gave a solution containing 4.29 per cent by weight of the carbonate, the two duplicate determinations agreeing exactly. But on longer standing and addition of more carbonate, the salt content rose to 5.54 and 5.74 per cent. In the course of the determination of the upper quadruple point (anhydrous salt, hydrate, liquid, vapor) the alcohol and salt content of two solutions was determined by analysis. One contained 90.96 per cent alcohol and 1.98 per cent salt by weight, and the other 94.74 per cent alcohol and 4.39 per cent salt (93.67 and 98.91 gm. alcohol per 100 gm. solvent, respectively).

The determination of this upper quadruple point, by dehydration of about 90 per cent methyl alcohol by successive treatments with the ignited and pulverized carbonate, showed that at that point the solvent is 99.35 per cent alcohol and the solution contains 94.14 per cent alcohol, 0.33 per cent water, and 5.53 per cent potassium carbonate by weight. These determinations have been plotted in the proper places in the figure. A determination made

by the distillation of an alcoholic solution, and determination of both alcohol and carbonate is also plotted. (Carbonate 4.41, water 20.76 and alcohol 74.83 per cent by weight of the solution.)

Since the lower or watery layer at the quadruple point Q_1 contains 6.1 per cent of alcohol and only 49.05 per cent carbonate, while the saturated solution of the carbonate, prepared from the same salt and standing at room temperature with an excess of the hydrate, contained 53.06 per cent of the salt, attempts were made to get determinations showing points on the line

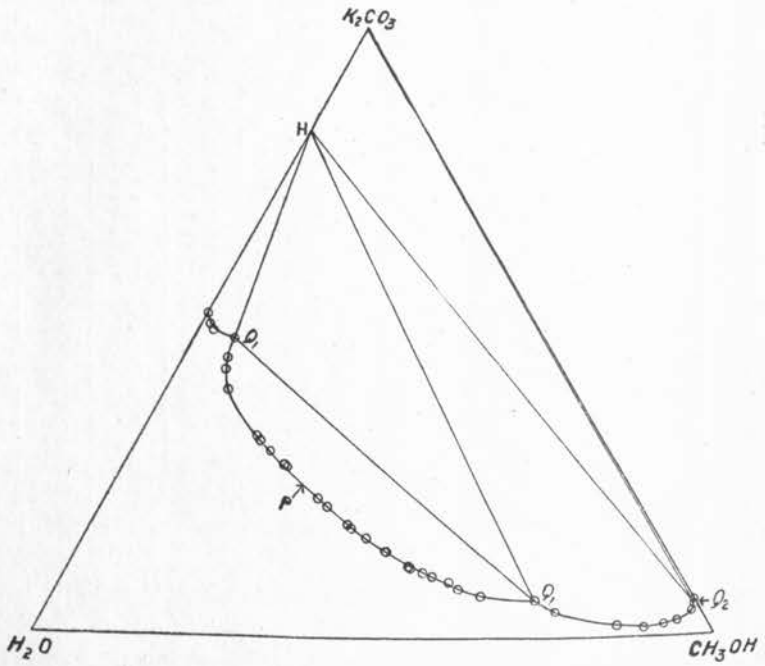

Figure 9. Equilibrium in the System: Potassium Carbonate, Methyl Alcohol, Water.

DE (fig. 2), and the two determinations marked with a star in table 8 were the result. They were made by the same general method as the other determinations in the table, except that the solution was not saturated with alcohol, only a small amount being added, and then water cautiously added, with shaking and standing, until the precipitated carbonate was just redissolved. As this point could not be determined with very great accuracy, the results are only approximate, but care was taken to get them as accurate as possible. They have been plotted on the figure.

SYSTEM POTASSIUM FLUORIDE, PROPYL ALCOHOL, WATER

The binodal curve was determined at room temperature as in the other systems, and the results are found in table 9 and plotted in figures 10 and 13. Experiments showed that the influence of temperature on the position of the binodal curve was quite marked in all cases in which propyl alcohol was one of the components of the system. Therefore some observations on the effect of such changes at several points in the curve were made, and are discussed under a later heading (Temperature Coefficients and Critical So-

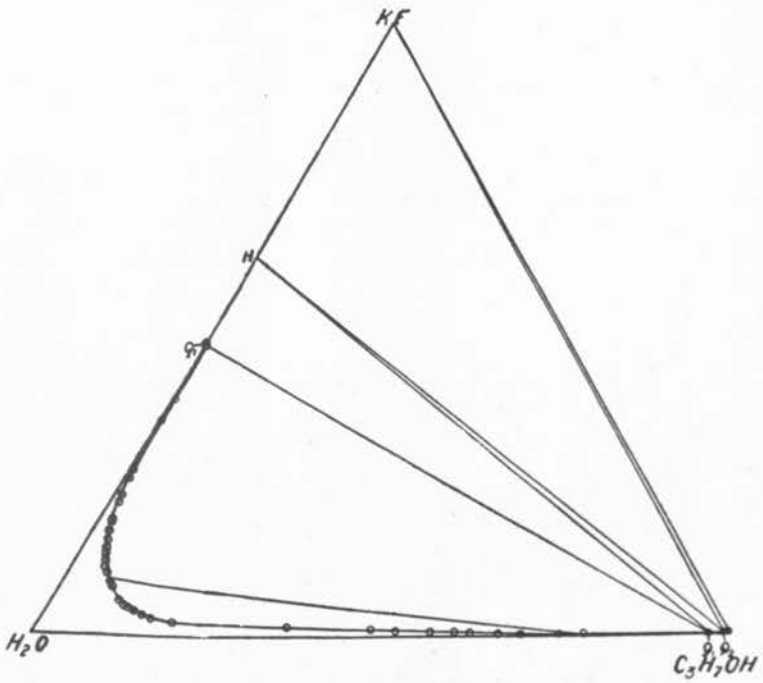

Figure 10. Equilibrium in the System: Potassium Fluoride, Normal Propyl Alcohol, Water.

lution Temperatures). Determinations of the composition of the two liquid layers in equilibrium at the quadruple point were made as in the other systems, and the lower solution was found to contain 47.62 per cent potassium fluoride and 0.039 per cent propyl alcohol by weight, or 90.91 and 0.075 gm. per 100 gm. solvent respectively. The upper solution contained 96.78 per cent propyl alcohol and 0.17 per cent potassium fluoride by weight, or 96.98 and 0.17 gm. per 100 gm. solvent respectively. A determination of the solubility of potassium fluoride in 99.6 per cent propyl alcohol, using about

45 gm. of the solution, showed that the saturated solution at room temperatures contained 0.34 per cent of the anhydrous fluoride. One tie-line was investigated, the upper solution by analysis containing 78.91 per cent of the alcohol and 0.31 per cent fluoride by weight, while the lower solution contaned 9.67 per cent fluoride by weight. This tie-line has been drawn on figure 10.

A determination of the composition of the liquid layer at the second quadruple point, where the liquid is in equilibrium with both the solid salt

TABLE 9

Binodal Curve for the System: Water, Propyl Alcohol, Potassium Fluoride, at room temperature. 86.77 per cent alcohol used in first two series, 98.05 per cent in the rest.

Solvent added		Total weight present			Grams per 100 gm. solvent			Per cent by weight		
Water	C_3H_7OH	KF	H_2O	C_3H_7OH	KF	H_2O	C_3H_7OH	KF	H_2O	C_3H_7OH
81.992	.956	28.891	82.118	.830	34.830	99.00	1.00	25.83	73.43	.74
11.242	.481	28.891	93.424	1.247	30.517	98.68	1.32	23.38	75.61	1.01
7.692	.477	28.891	101.179	1.661	28.093	93.38	1.62	21.93	76.80	1.26
16.289	1.123	28.891	117.616	2.636	24.025	97.81	2.19	19.37	78.86	1.77
4.593	.322	28.891	122.252	2.915	23.082	97.67	2.33	18.75	79.35	1.89
13.514	1.249	28.891	135.932	3.998	20.647	97.14	2.86	17.11	80.52	2.37
14.112	1.401	28.891	150.226	5.217	18.586	96.64	3.36	15.67	81.49	2.83
17.346	2.082	28.891	167.844	7.027	16.521	95.98	4.02	14.18	82.37	3.45
9.462	1.056	28.891	177.446	7.943	15.584	95.72	4.28	13.48	82.81	3.70
19.632	2.804	28.891	197.444	10.381	13.902	95.00	5.00	12.21	83.41	4.39
18.869	2.715	28.891	216.673	12.736	12.594	94.45	5.55	11.19	83.89	4.93
23.355	3.759	28.891	240.527	15.996	11.262	93.76	6.24	10.12	84.27	5.61
15.218	.159	5.736	15.240	.137	37.303	99.11	.89	27.17	72.18	.65
4.063	.188	5.736	19.328	.300	29.224	98.47	1.53	22.62	76.20	1.18
3.754	.231	5.736	23.112	.501	24.292	97.88	2.12	19.54	78.75	1.71
8.190	.864	5.736	31.416	1.251	17.559	96.17	3.83	14.94	81.81	3.26
4.101	.543	5.736	35.589	1.722	15.374	95.38	4.62	13.33	82.67	4.00
12.350	1.963	5.736	48.199	3.425	11.111	93.37	6.63	10.00	84.03	5.97
*5.920	1.091	5.736	54.241	4.370	9.787	92.54	7.46	8.91	84.29	6.80
5.004	1.034	5.736	59.382	5.267	8.873	91.85	8.15	8.15	84.36	7.49
22.201	4.931	5.736	82.235	9.546	6.250	89.60	10.40	5.88	84.33	9.79
4.073	1.105	5.736	86.454	10.505	5.916	89.17	10.83	5.59	84.19	10.22
4.020	1.119	5.736	90.622	11.476	5.618	88.76	11.24	5.32	84.04	10.64
10.944	3.112	5.736	101.978	14.176	4.938	87.80	12.20	4.71	83.67	11.62
13.259	4.006	5.736	115.767	17.652	4.299	86.77	13.23	4.12	83.19	12.69
13.831	5.334	5.736	130.303	22.281	3.759	85.40	14.60	3.62	82.30	14.07
17.434	7.202	5.736	148.690	28.530	3.237	83.90	16.10	3.14	81.27	15.59
29.250	17.561	5.736	180.263	43.768	2.560	80.46	19.54	2.50	78.45	19.05
46.619	.124	29.873	46.621	.122	63.908	99.74	.26	38.99	60.85	.16
7.734	.073	29.873	54.356	.194	54.762	99.64	.36	35.38	64.38	.23
83.016	3.506	29.873	137.440	3.632	21.175	97.43	2.57	17.47	80.40	2.12
15.696	2.054	.909	15.736	2.014	5.121	88.65	11.35	4.87	84.33	10.80
30.588	24.849	1.315	46.809	26.378	1.797	63.96	36.04	1.77	62.83	35.40
5.067	22.512	1.315	52.315	48.451	1.305	51.92	48.08	1.29	51.25	47.46
2.582	10.721	1.315	55.106	58.963	1.153	48.31	51.69	1.14	47.76	51.10
4.255	20.316	1.315	59.757	78.883	.948	43.10	56.90	.94	42.70	56.36
3.335	18.504	1.315	63.453	97.026	.819	39.54	60.46	.81	39.22	59.97
2.413	14.205	1.315	66.143	110.954	.743	37.35	62.65	.74	37.07	62.19
(Part of	above)	.548	27.541	46.197	.743	37.35	62.65	.74	37.07	62.19
1.589	12.919	.548	29.382	58.864	.621	33.30	66.70	.62	33.09	66.29
1.713	14.047	.548	31.366	72.640	.527	30.16	69.84	.52	30.00	69.47
3.225	36.306	.548	35.299	108.238	.382	24.59	75.41	.38	24.50	75.12
(Distillation)		.....	.....	.....	.310	20.34	79.66	.31	21.19	78.91

*Loss on standing .024 gm.

and its hydrate, was made with the original alcohol, and the distillate was found to be 98.72 per cent by weight propyl alcohol. Later another determination was made, using some of the propyl alcohol recovered and fractionated as described on page 14, and diluted with water. After digesting with an excess of fluoride the distillate contained 98.77 and 98.73 per cent of alcohol by weight. The solution was found to contain 0.28 per cent by

weight of the anhydrous fluoride, and its composition was thus: propyl alcohol 98.44 per cent, potassium fluoride 0.28 per cent, water 1.28 per cent by weight. The close agreement of the two determinations made on the recovered and purified alcohol with the one made with the original alcohol, indicates that the influence of the impurities in the latter was negligible.

SYSTEM POTASSIUM CARBONATE, PROPYL ALCOHOL, WATER

The determinations of points on the binodal curve were made as in the other systems, and are found in table 10, and plotted in figures 11 and 13.

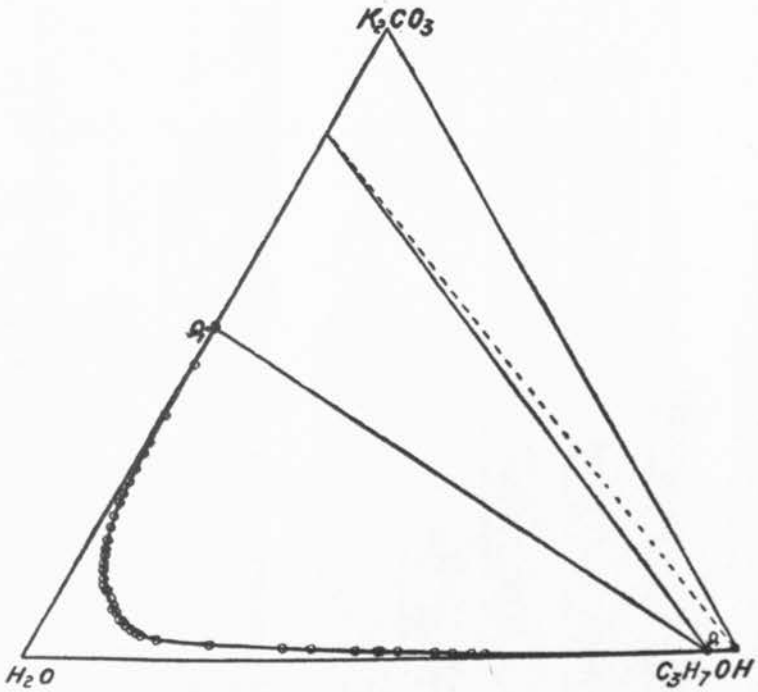

Figure 11. Equilibrium in the System: Potassium Carbonate, Normal Propyl Alcohol, Water.

The temperature of the solutions was frequently tested during each series of determinations, and kept between 22 and 26°. Some determinations of the effect of change of temperature on the position of the binodal curve were made, and are discussed later. Duplicate determinations of the amount of carbonate in the lower solution at the quadruple point gave 53.05 and 52.89 per cent, or practically the same as in saturated solutions of the carbonate

at room temperatures (53.06 per cent). A determination of the propyl alcohol content, in the distillate from about 300 gm. of the solution, showed this to be only 0.02 per cent by weight. The upper solution contained 0.017 per cent by weight of the carbonate, and 95.83 per cent of propyl alcohol. It will be noted that as in the case of the quadruple point determinations with ethyl alcohol, the upper layer in the system containing potassium carbonate is a weaker alcohol than in the system containing the fluoride. This indicates,

TABLE 10

Binodal Curve for System: Water, Propyl Alcohol, Potassium Carbonate, at room temperature, 98.05 per cent propyl alcohol used.

Solvent added		Total weight present			Grams per 100 gm. solvent			Per cent by weight		
Water	Alcohol	K_2CO_3	H_2O	C_3H_7OH	K_2CO_3	H_2O	C_3H_7OH	K_2CO_3	H_2O	C_3H_7OH
28.588	.065	25.387	28.589	.064	88.602	99.78	.22	46.98	52.91	.12
10.990	.063	25.387	39.580	.126	63.937	99.68	.32	39.00	60.80	.20
8.246	.067	25.387	47.827	.192	52.869	99.60	.40	34.58	65.15	.26
3.697	.079	25.387	51.526	.269	49.014	99.48	.52	32.89	66.76	.35
6.136	.103	25.387	57.664	.370	43.745	99.36	.64	30.43	69.12	.45
6.085	.159	25.387	63.752	.526	39.496	99.18	.82	28.31	71.10	.59
5.864	.225	25.387	69.620	.747	36.078	98.94	1.06	26.51	72.71	.78
5.524	.235	25.387	74.149	.977	33.349	98.72	1.28	25.01	74.03	.96
9.286	.503	25.387	84.445	1.470	29.544	98.29	1.71	22.81	75.87	1.32
9.500	.708	25.387	93.759	2.164	26.466	97.74	2.26	20.93	77.29	1.79
10.833	.926	25.387	104.611	3.071	23.576	97.15	2.85	19.08	78.62	2.31
*10.789	1.015	25.387	115.395	4.065	21.251	96.60	3.40	17.53	79.67	2.80
9.479	.993	25.387	124.894	5.038	19.539	96.12	3.88	16.35	80.41	3.24
9.920	1.039	25.387	134.834	6.057	18.019	95.70	4.30	15.27	81.09	3.64
9.491	1.059	25.387	144.346	7.095	16.764	95.32	4.68	14.36	81.63	4.01
10.416	1.243	25.387	154.786	8.314	15.565	94.90	5.10	13.47	82.12	4.41
7.552	1.046	25.387	162.359	9.339	14.786	94.56	5.44	12.88	82.38	4.74
15.407	2.165	25.387	177.808	11.462	13.413	93.94	6.06	11.83	82.83	5.34
(Part of	above)	10.593	74.191	4.786	13.413	93.94	6.06	11.83	82.83	5.34
5.583	1.250	10.593	79.798	6.012	12.345	92.99	7.01	10.99	82.77	6.24
10.665	2.071	10.593	90.503	8.043	10.749	91.84	8.16	9.71	82.93	7.37
12.445	2.298	10.593	102.993	10.296	9.350	90.91	9.09	8.55	83.14	8.31
15.301	2.984	10.593	118.352	13.222	8.051	89.95	10.05	7.45	83.25	9.30
28.767	6.540	10.593	147.247	19.634	6.348	88.23	11.77	5.97	82.96	11.07
22.963	1.193	3.986	22.986	1.170	16.501	95.16	4.84	14.16	81.68	4.15
6.953	1.045	3.986	29.959	2.195	12.397	93.17	6.83	11.03	82.89	6.08
11.429	2.059	3.986	41.428	4.214	8.733	90.77	9.23	8.03	83.49	8.49
9.889	2.142	3.986	51.359	6.314	6.911	89.05	10.95	6.46	83.29	10.24
9.429	2.275	3.986	60.832	8.545	5.745	87.68	12.32	5.43	82.92	11.65
8.694	2.210	3.986	69.569	10.712	4.965	86.66	13.34	4.73	82.56	12.71
† 7.671	2.217	3.986	77.267	12.881	4.422	85.71	14.29	4.23	82.08	13.68
6.919	2.252	3.986	84.230	15.089	4.013	84.81	15.19	3.86	81.54	14.60
17.689	7.022	3.986	102.056	21.974	3.214	82.28	17.72	3.11	79.71	17.17
17.495	19.055	3.986	119.923	40.657	2.482	74.68	25.32	2.42	72.87	24.71
8.533	13.177	3.986	128.713	53.577	2.187	70.61	29.39	2.14	69.10	28.76
2.889	19.706	3.986	131.986	72.899	1.945	64.42	35.58	1.91	63.19	34.90
5.891	18.412	3.986	138.236	90.952	1.739	60.32	39.68	1.71	59.29	39.00
(Part of	above)	1.463	50.759	33.391	1.739	60.32	39.68	1.71	59.29	39.00
7.092	16.872	1.463	58.180	49.934	1.353	53.81	46.19	1.33	53.09	45.57
7.287	14.163	1.463	65.743	63.821	1.129	50.74	49.26	1.116	50.17	48.71
7.154	15.950	1.463	73.208	79.460	.958	47.95	52.05	.948	47.49	51.56
(Part of	above)	.464	23.211	25.193	.958	47.95	52.05	.948	47.49	51.56
5.454	14.017	.464	28.938	38.937	.684	42.63	57.37	.679	42.34	56.98
3.797	10.543	.464	32.940	49.275	.564	40.07	59.93	.561	39.85	59.59
4.606	13.986	.464	37.819	62.988	.460	37.52	62.48	.457	37.35	62.19
4.399	14.334	.464	42.498	77.042	.388	35.55	64.45	.387	35.41	64.20

*Loss on standing .026 gm.
†Loss on standing .021 gm.

as previously shown, that the saturated solution of the fluoride has a lower vapor tension than that of the carbonate. Determination of the solubility of the anhydrous carbonate in 99.6 per cent propyl alcohol showed that the saturated solution under ordinary conditions contained 0.031 per cent of the salt. The fluoride is therefore ten times as soluble as the carbonate both in absolute propyl alcohol, and at their respective quadruple points.

The other quadruple point, where there are two solid phases, a liquid and a gaseous phase, was not determined, as from the known vapor pressure of the hydrate of the salt, this point would undoubtedly lie within a few tenths of a per cent of 100 per cent alcohol, and unless a quantity of specially pure alcohol was available, so that the actual gravity of the absolutely pure alcohol, carefully dried, could be obtained, it would be a waste of time to attempt the determination of this point.

SYSTEM SODIUM CHLORIDE, PROPYL ALCOHOL, WATER

As an example of a salt only moderately soluble in water, not capable of crystallizing with water of crystallization, and possessing obviously a low affinity for water, sodium chloride was chosen as the precipitant to compare with potassum carbonate and fluoride. The binodal curve was determined as in the other systems, and the determinations are found in table 11, and plotted in figures 12 and 13. The first three series of determinations were made at room temperature, but without taking special care to control this

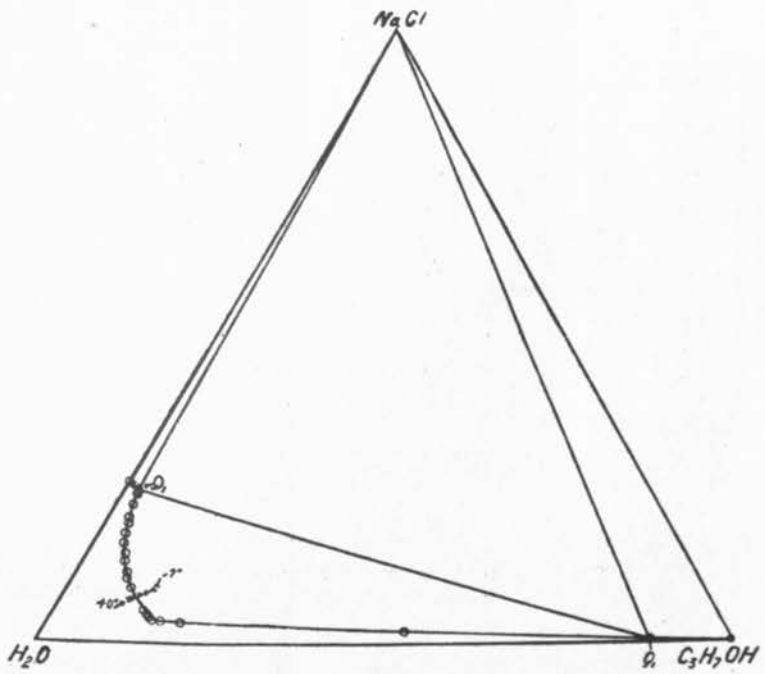

Figure 12. Equilibrium in the System: Sodium Chloride, Normal Propyl Alcohol, Water.

factor. In the last series, containing the solutions high in alcohol, where the temperature would exert an influence that might be very disturbing, it was determined frequently, and kept between 23° and 25°. The fact that those determinations in this series which fall within the limits of concentration covered by the other two series check well with them would indicate that the temperature in these series was not seriously different from that assumed. (23 to 26°). As we do not have in the case of sodium chloride the relatively large heat of dilution which is found with the other two salts, the

TABLE 11

Binodal Curve for System: Sodium Chloride, Propyl Alcohol, Water, at room temperature. 98.05 per cent propyl alcohol used.

Solvent added		Total weight present			Grams per 100 gm. solvent			Per cent by weight		
Water	Alcohol	NaCl	H_2O	C_3H_7OH	NaCl	H_2O	C_3H_7OH	NaCl	H_2O	C_3H_7OH
33.790	1.200	10.258	33.813	1.177	29.317	96.64	3.36	22.67	74.72	2.60
6.161	.620	10.258	39.986	1.785	24.558	95.73	4.27	19.72	76.86	3.43
7.259	.892	10.258	47.262	2.660	20.548	94.67	5.33	17.05	78.53	4.42
8.690	1.220	10.258	55.976	3.856	17.145	93.56	6.44	14.64	79.87	5.50
8.818	1.467	10.258	64.823	5.294	14.630	92.45	7.55	12.76	80.65	6.58
6.995	1.219	10.258	71.842	6.489	13.096	91.72	8.28	11.58	81.10	7.32
10.747	1.942	10.258	82.627	8.393	11.270	90.78	9.22	10.13	81.59	8.29
10.461	2.263	10.258	93.132	10.612	9.888	89.77	10.23	9.00	81.69	9.31
20.378	.813	5.529	20.394	.797	26.091	96.24	3.76	20.69	76.33	2.98
3.982	.439	5.529	24.385	1.227	21.589	95.21	4.79	17.76	78.30	3.94
8.667	1.172	5.529	33.075	2.376	15.596	93.30	6.70	13.49	80.71	5.80
8.913	1.383	5.529	42.015	3.732	12.086	91.84	8.16	10.78	81.94	7.28
61.778	1.828	20.636	61.814	1.792	32.443	97.18	2.82	24.50	73.37	2.13
7.425	.656	20.636	69.252	2.435	28.786	96.60	3.40	22.35	75.01	2.64
9.318	.931	20.636	78.588	3.348	25.186	95.91	4.09	20.12	76.61	3.27
10.504	1.052	20.636	89.113	4.379	22.072	95.32	4.68	18.08	78.09	3.83
10.549	1.284	20.636	99.687	5.638	19.593	94.65	5.35	16.38	79.14	4.47
6.671	1.221	20.636	106.382	6.835	18.227	93.96	6.04	15.42	79.47	5.11
9.445	1.231	20.636	115.851	8.042	16.656	93.51	6.49	14.28	80.16	5.56
8.847	1.218	20.636	124.722	9.236	15.405	93.11	6.89	13.35	80.68	5.97
13.476	2.036	20.636	138.238	11.232	13.806	92.49	7.51	12.13	81.27	6.60
10.895	1.839	20.636	149.169	13.035	12.722	91.96	8.04	11.29	81.58	7.13
9.878	1.962	20.636	159.085	14.959	11.857	91.41	8.59	10.60	81.72	7.68
25.455	4.246	20.636	184.623	19.122	10.128	90.61	9.39	9.20	82.28	8.52
25.046	1.345	5.606	25.072	1.319	21.242	95.00	5.00	17.52	78.36	4.12
6.186	.797	5.606	31.274	2.100	16.797	93.71	6.29	14.38	80.23	5.39
6.022	.936	5.606	37.314	3.018	13.900	92.52	7.48	12.20	81.23	6.57
6.333	1.164	5.606	43.670	4.159	11.721	91.30	8.70	10.49	81.72	7.79
6.630	1.084	5.606	50.321	5.222	10.093	90.60	9.40	9.17	82.29	8.54
7.124	1.418	5.606	57.473	6.612	8.748	89.68	10.32	8.04	82.47	9.49
9.762	2.307	5.606	67.280	8.874	7.361	88.35	11.65	6.86	82.29	10.85
9.194	2.396	5.606	76.521	11.223	6.389	87.21	12.79	5.95	81.23	11.91
10.611	2.405	5.606	87.179	13.581	5.563	86.52	13.48	5.27	81.96	12.77
*10.003	2.541	5.606	97.154	16.060	4.952	85.81	14.19	4.72	81.76	13.52
8.512	2.340	5.606	105.712	18.354	4.519	85.21	14.79	4.32	81.53	14.15
10.978	2.917	5.606	116.747	21.214	4.063	84.62	15.38	3.90	81.32	14.78
2.275	2.809	5.606	119.077	23.968	3.919	83.24	16.76	3.77	80.10	16.13
2.941	6.100	5.606	122.137	29.949	3.686	80.31	19.69	3.55	77.46	18.99
† .889	112.002	6.042	125.210	139.767	2.280	47.25	52.75	2.23	46.20	51.57

*Loss on standing .090 gm.

†During this determination it was necessary to add .436 gm. of salt in order to cause separation into two liquid phases, as the addition of the alcohol alone, even in large quantities, did not cause separation. Temperature of this determination 23°.

only factor tending to raise the temperature unduly was the heat of the hands, and the effect seems to have been negligible.

Determinations of the effect of temperature on the equilibrium showed that this is a much greater factor than in the case of the other two salts. This will be discussed in detail under the next head.

There is only one quadruple point in this system, as the salt is not capable of forming a hydrate at ordinary temperatures, and there can therefore be

but one solid phase. The composition of the two liquid layers at this point was determined as in the other similar cases. Three determinations of the propyl alcohol content of the lower layer showed 2.29, 2.95 and 2.21 per cent respectively. Determinations of the salt content gave 24.81 and 25.00 per cent as against a content of 26.33 per cent of salt in the saturated solution in pure water under the same conditions. Duplicate determinations on

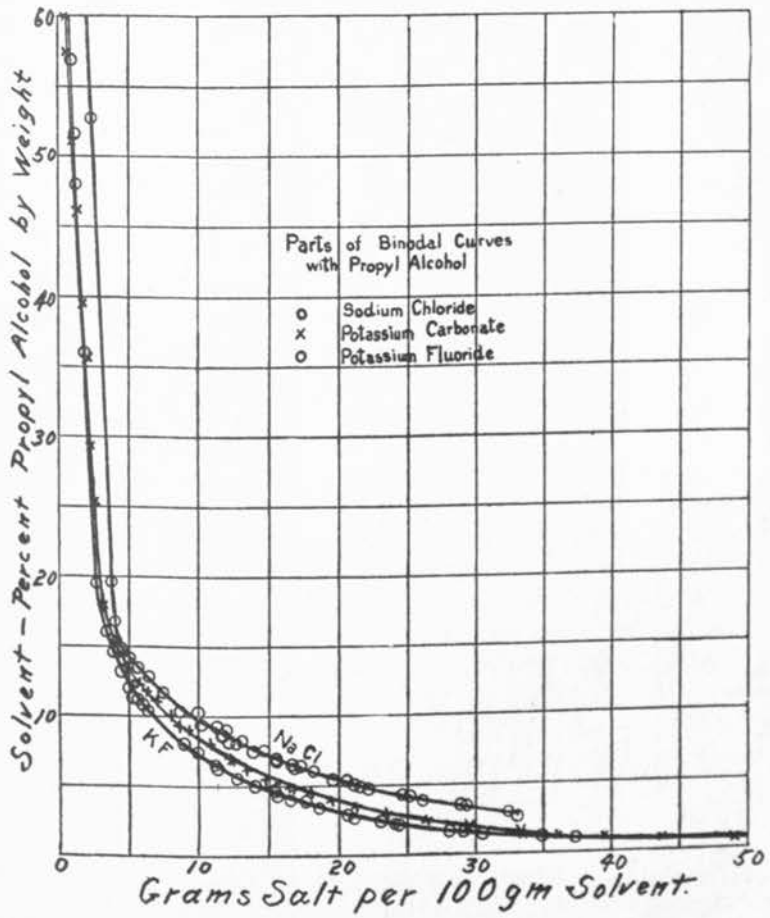

Figure 13.

the upper layer gave 87.81 and 87.59 per cent alcohol, and 0.53 and 0.56 per cent salt by weight, or 88.28 and 88.08 gm. alcohol per 100 gm. solvent. A determination of the composition of a saturated solution of salt in 99.6 per cent propyl alcohol, showed that it contained 0.040 per cent of salt by weight. In this case the solubility decreases continuously with the increase in strength of the alcohol.

Two determinations on the line (DE, fig. 2) joining the saturated solution of the salt in water with the lower solution at the quadruple point have been made by Armstrong and Eyre,[1] in the course of their work on the displacement of salts from solution by various precipitants. Their salt was a little more soluble in water than mine (36.295 gm. per 100 gm. water, forming a solution containing 26.63 per cent salt), but the difference is so small as to be invisible on the plot, so their results have been marked with crosses on figure 12. They found that one solution saturated with salt, contained one-fourth gram molecule propyl alcohol per 1,000 gm. water and 355.75 gm. salt, while another contained one-half gram molecule of propyl alcohol per 1,000 gm. water and 350.20 gm. salt. These two solutions would then have the composition: propyl alcohol 1.09 and 2.17 per cent, water 72.95 and 72.45 per cent, sodium chloride 25.95 and 25.37 per cent respectively, and are plotted in figure 12.

Parts of the binodal curves for the three systems involving propyl alcohol have been drawn in rectangular coördinates in figure 13. It will be noticed that the curves are in general parallel, but the curve for the carbonate lies above that for the fluoride at concentrations from three to forty grams of salt per 100 gm. solvent, and below it for concentrations outside these limits. This is exactly the reverse of things shown in the systems involving ethyl alcohol (fig. 4), and would indicate that the relative salting-out power of different salts depends to a certain extent upon the substance treated, and not, as some authors have stated, entirely upon the anion and cathion of the salt. The fact that sodium chloride, which is here shown to be almost as good a salting-out reagent as potassium carbonate, for propyl alcohol, does not salt out ethyl alcohol at all, although it is relatively insoluble in the strong alcohol, is another indication that we cannot reason from a few isolated cases to form a general theory of the salting-out process.

TEMPERATURE COEFFICIENTS AND CRITICAL SOLUTION TEMPERATURES

By the critical solution temperature of a mixture, we understand that temperature at which the solution just becomes homogeneous. We may then distinguish between upper and lower critical temperatures. An upper critical solution temperature is found when on warming an inhomogeneous mixture complete miscibility is obtained at and above a certain temperature, while a lower critical temperature is one below which the solution is homogeneous, but above which it separates into two layers. For ternary systems, the general theory of the critical solubility temperatures has been given by

[1] Proc. Roy. Soc. (A), **84**, 123.

Timmermans.[1] He considers that all liquid pairs have both an upper and a lower critical solution temperature. Above the former and below the latter temperature they are miscible. Many examples of liquid pairs having upper critical temperatures are known, and some that have lower critical temperatures. But in the case that only one of these temperatures is experimentally realizable for a given pair, it is probable that the other lies either above the boiling point or below the freezing point of the mixture. By the addition of certain substances, very soluble in both components, it was possible in some cases to raise the lower critical temperature and lower the upper one so that both became realizable.

For the case of two solutions which are miscible in all proportions at all temperatures, Timmermans assumes that the lower critical solution temperature lies above the upper critical solution temperature, and therefore there can be no temperature above the lower critical temperature which is at the same time below the upper critical temperature, and vice versa. For this reason such liquids are miscible at all temperatures. However, these liquid pairs should actually have such critical temperatures, which might be realized, if we could add some substance, soluble in only one of the liquids, which would lower the lower critical solution temperature or raise the upper one, or both. Such a substance would cause a separation of the homogeneous mixture into two liquid phases, i. e., would "salt out" the liquid. The systems described herein belong to this class. It seemed, therefore, interesting to study the effect of change of temperature on some of them, and a few experiments along this line were performed, and will be described here.

It is to be noticed that the theoretical requirement that the salting-out substance be insoluble in one of the liquids appears to refer only to a relative solubility, since in the systems involving methyl and ethyl alcohol, the salting-out substances here studied are certainly soluble, and in the case of methyl alcohol and potassium carbonate, this solubility reaches a value of over 6 gm. per 100 gm. solvent in the absolute alcohol. If the statement in the theory be amended to read that the substance capable of salting out a liquid must have only a slight solubility in mixtures containing a large proportion of that liquid, it would be in better accord with the facts.

For the system: potassium carbonate, ethyl alcohol, water, Cuno[2] has shown that the different isotherms representing the binodal curve all cross at or near the plait-point, and that this point would then be independent of the temperature, and a solution at this point would not cloud (become inhomogeneous) on either warming or cooling. Solutions containing more alcohol than this critical solution will cloud on cooling but remain clear on heating (i. e., are at their upper critical temperature), while those with less alcohol cloud on warming but remain clear on cooling (showing them to be at their

[1] Z. phys. Chem., **58**, 129.
[2] Ann. Physik, **25**, 346.

lower critical temperature). This idea as to the plait-point is supported by the observations of Krug and McElroy,[1] who studied the precipitation of acetone by the sugars, and state that the isotherms in the system: acetone, dextrose, water, all cross each other in one point. The observations of Traube and Neuberg,[2] in the system: ammonium sulphate, ethyl alcohol, water, also bear out the statement. They state that warming the lower one of two conjugate solutions always causes it to separate, but cooling it does not. With the upper layer these results are reversed. This corresponds exactly with the case of the carbonate.

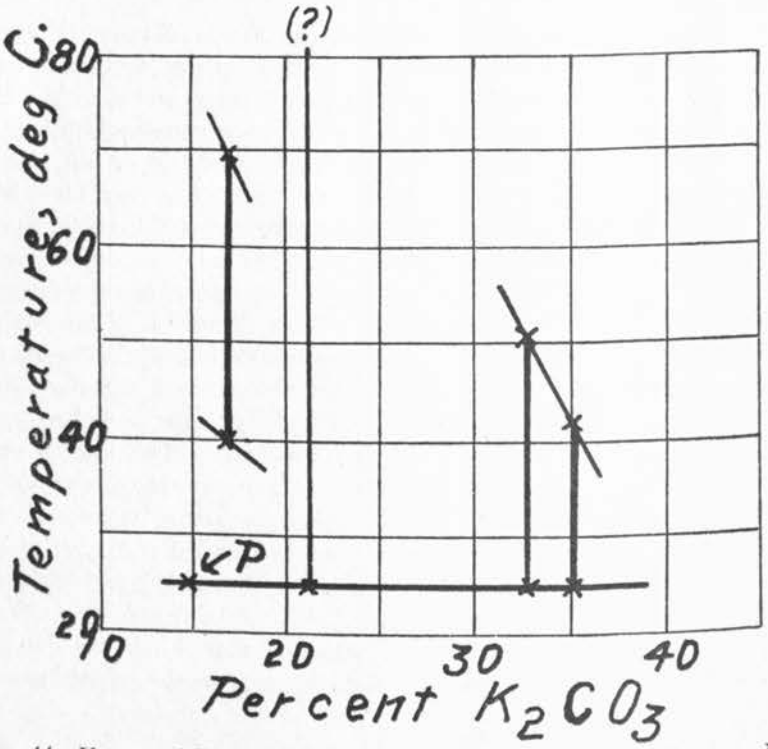

Figure 14. Upper and Lower Critical Solution Temperatures in the System: Potassium Carbonate, Ethyl Alcohol, Water.

But Cuno also found that in the case of solutions with less alcohol than that at the plait-point, when some of them were heated to a higher temperature they cleared again, so exhibiting both upper and lower critical temperatures. Thus with a solution containing 35.19 per cent of carbonate by weight, the solution was inhomogeneous between the temperatures 25° and 42°, while another solution containing 32.85 per cent of the salt was in-

[1] J. Analyt. Appl. Chem., 1892, **6**, 153, 188.
[2] Z. phys. Chem., 1887, **1**, 509.

homogeneous between 25° and 51°. A solution with 21.16 per cent salt was clear below 25°, but cloudy from that point up to 80°, which was as high as it could be tested. Therefore, with increasing salt content, in the upper layer the temperature interval between the upper and lower critical temperatures for a given solution decreases, as does also the alcohol content of the solution. Snell[1] showed that a solution containing 16.8 per cent carbonate, 16.8 per cent alcohol, and 66.4 per cent water had a lower critical solution temperature of 40° and an upper one of 70°. This is very close to the plait-point as given by Cuno (30 gm. alcohol, 22.5 gm. carbonate, and

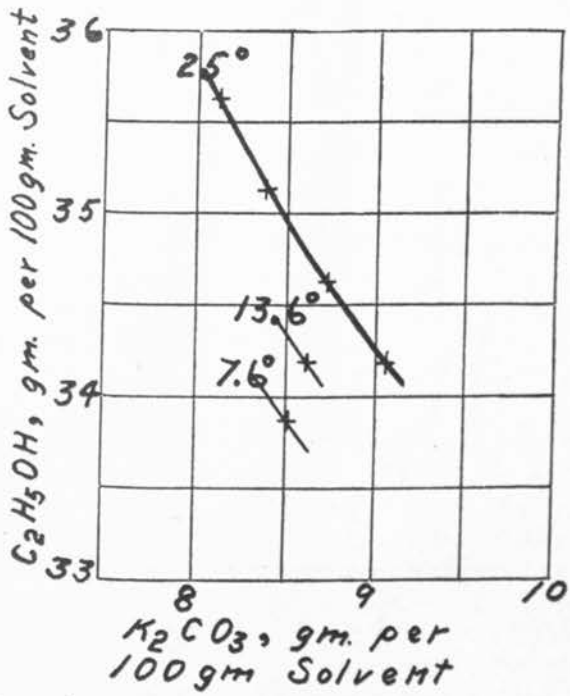

Figure 15. Isotherms in the System: Potassium Carbonate, Ethyl Alcohol, Water.

100 gm. water, or 14.75 per cent carbonate), and would tend to throw doubt on the latter's statement that the isotherms all cross at the plait-point. These determinations have been plotted in figure 14, the two temperatures at which the solution just clears being joined. The plait-point is also indicated, and the apparent locus of the upper critical temperature for solutions having a lower critical temperature of 25°.

At the close of the third series of determinations in table 6, the solution (containing 8.03 per cent carbonate, and therefore one of the upper layers

[1] J. Phys. Chem., 1898, **2**, 457.

of a pair of conjugate solutions) was found to have an upper critical temperature of 24.8°. It was now cooled and water added until clear. This solution, having the composition 8.625 gm. potassium carbonate, 65.81 gm. water and 34.19 gm. alcohol per 100 gm. solvent, had an upper critical temperature of 13.6°. On cooling more, and adding water to clear, a solution having an upper critical temperature of 7.6° was obtained. It contained 8.554 gm. carbonate, 66.13 gm. water, and 33.87 gm. alcohol per 100 gm. solvent. These two points lie on the isotherms for those temperatures. In figure 15 the isotherm for 25° at that concentration has been plotted from the results in table 6, and these two results put in and the general course of their isotherms at that concentration sketched.

In the system: potassium fluoride, ethyl alcohol, water, no work has previously been done. In preliminary work here, several solutions which were just homogeneous were both heated and cooled without noticeable separation into two layers. The only quantitative work thus far done along this line on the system was in connection with the determination of alcohol mentioned on page 24, where, at a fluoride concentration of 15.805 gm. per 100 gm. solvent, a lower critical temperature was shown, and the solution clouded slightly on heating. The amount of solvent present (about 46 gm.) was so small that no very accurate determination of the effect of temperature was possible, but as near as could be told, the addition of 0.25 cc. water restored the solution to homogeneity at 35°. The effect of a change of temperature on the binodal curve appears to be small.

In the system: potassium carbonate, methyl alcohol, water, B. de Bruyn,[1] by determining the location of the quadruple point Q_1 (solid, two liquids, vapor) at various temperatures, has concluded that as the temperature is lowered, the composition of the two liquid layers at the quadruple point becomes more nearly alike, until at about —35° they become identical, and hence below this temperature the mixture can contain but one liquid phase, i. e., this is the lower limit of the lower critical solution temperature. He has determined the isotherms in this system for several temperatures, and does not find that they cross at all. From his results for the quadruple points, such isotherms would have to cross each other twice, if they crossed at all. It therefore appears that it is not necessary that the plait-point have this peculiar property in all cases.

I took some of the upper solution at the critical point in this system, and verified qualitatively de Bruyn's results. Cooling this solution caused no separation, but on heating it clouded at 24.5°. Addition of a small amount of an aqueous solution of potassium carbonate having the same percent of carbonate as this solution, raised the point of clouding to about 36°. On heating to higher temperatures, the solution cleared up a good deal, becom-

[1] Z. phys. Chem., **32**, 63.

ing almost clear at 68°, where it was about to boil. In the heating and cooling of this solution the phenomenon of the supersaturation of the upper layer was frequently observed, and it could be supercooled a couple of degrees before the separation took place, if the cooling was rapidly done. A further addition of a little of the same aqueous carbonate solution caused the solution to remain clear even when heated to 62°.

The three systems involving propyl alcohol appear never to have been studied before, and it was here that the effect of temperature appeared to be the greatest. In the system: potassium fluoride, propyl alcohol, water, at the close of the third series (table 9) the solution was cooled below zero, and no cloudiness appeared. Propyl alcohol was now added, a little at a time, and a solution formed having the composition: potassium fluoride 21.003, water 96.65 and propyl alcohol 3.35 gm. per 100 gm. solvent, and a lower critical temperature of —3° C. Thus with practically no change in salt

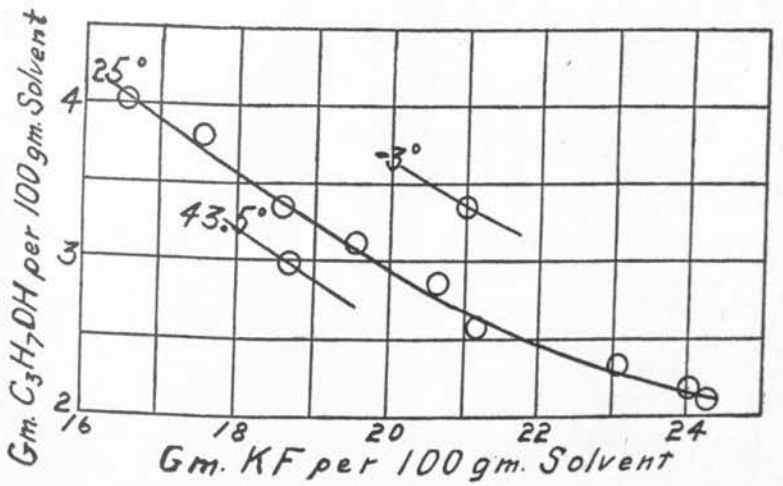

Figure 16. Isotherms in the System: Potassium Fluoride, Normal Propyl Alcohol, Water.

content (from 21.175 to 21.003 gm. per 100 gm. solvent) the drop of 28.6° in temperature increased the solubility of the alcohol from 2.57 to 3.35 gm. per 100 gm. solvent. On warming, over 10 gm. of water had to be added to the solution (containing about 140 gm. solvent) to make the solution homogeneous, and this solution (fluoride 19.554, water 96.88 and propyl alcohol 3.12 gm. per 100 gm. solvent) had a lower critical temperature of 14°. As in the case investigated by B. de Bruyn, and mentioned above, the lower the temperature the greater the apparent effect on the position of the curve. This was well shown by the fact that upon now heating this solution only about 7 cc. of water needed to be added to give a solution (fluoride 18.693, water 97.02 and propyl alcohol 2.98 gm. per 100 gm. solvent) which had a

lower critical solution temperature of 43.5°. In figure 16, part of the isotherm for 25° (approximately) has been plotted from the data in table 9, and the points thus determined marked and the position of their isotherms indicated.

In the same system, with a solution much richer in alcohol, (fluoride 0.533, water 29.93 and propyl alcohol 70.07 gm. per 100 gm. solvent) a lower critical solution temperature of 27° and an upper one of 41.5° could be clearly found. Supercooling and superheating gave much trouble in this determination. The separation into two phases between the temperatures mentioned was very noticeable.

In the system: potassium carbonate, propyl alcohol, water, an attempt was made to determine the effect of temperature changes on the solubility of the alcohol in solutions having a constant salt content. That portion (about 105 gm) of the solution left at the end of the fourth series of determinations in table 10, and not used in the last series, was used in these determinations. It contained, as noted in table 10, 0.958 gm. potassium carbonate, 47.95 gm. water, and 52.05 gm. propyl alcohol per 100 gm. solvent. It had a lower critical temperature of 27.0° and an upper critical temperature of 57.3°. An aqueous solution was prepared, of the same carbonate content as this solution. About 0.5 gm. of this aqueous solution was now added to the alcoholic solution. The salt content of course remained unchanged, the composition of the solvent was now: water 48.28 per cent, alcohol 51.72 per cent, and the critical solution temperatures 34.5° and 50.9°. By accident, a little more of the water solution than was intended was now added (1.218 gm.) and the solvent in the resulting solution had the composition: water 48.87 and alcohol 51.13 per cent. On heating and cooling, the solution appeared to be homogeneous except for a trace of cloudiness noticed between 40° and 45°.

More carbonate, in the form of a solution of known strength, was now added, and the solution cooled to about —12° C., remaining cloudy all the time after the carbonate was added. Water at room temperature was added in small portions, and of course warmed the solution somewhat at each addition; after which it was again cooled. The purpose was to get a solution having a lower critical point at as low a temperature as possible, and take a series of critical temperatures, by adding small portions of water. During the addition of one portion of water, it was noticed that a part of the solution cleared up, but clouded again on cooling.

Suspecting the presence of a critical temperature, when further cooling did not clear this, it was allowed to warm up a little, when it was found to clear sharply at exactly —10°. Cooling below this produced copious cloudiness, and just at this point it would clear sharply. Careful observation failed to show any trace of crystallization or precipitation of a solid phase, the solution had the same appearance as at other times when at a critical

solution temperature. This appeared to be then an upper critical solution temperature, at —10°. On warming this solution carefully to 60°, no other cloudiness was noticed at any time. After weighing at 25°, some of the 98 per cent propyl alcohol was cautiously added until the solution just became cloudy. Over 18 grams was required, showing that the solution which had shown an upper critical point at —10° was far from being saturated at ordinary temperatures. As a matter of fact this solution had a composition of: carbonate 1.405 gm, water 59.60 gm., and alcohol 40.40 gm. per 100 gm. solvent, whereas from the results in table 10 it is seen that a solution on the binodal curve at room temperature, having that salt concentration, would have had about 45 per cent alcohol in the solvent. These and other results in this system are plotted in figure 17.

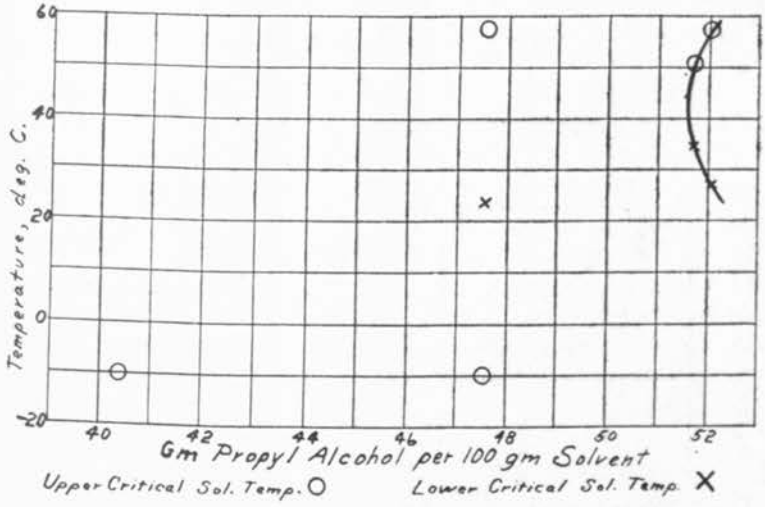

Figure 17. Upper and Lower Critical Solution Temperatures in the System: Potassium Carbonate, Normal Propyl Alcohol, Water.

After the addition of the alcohol, as above-mentioned, the solution contained 1.237 gm. carbonate, 52.43 gm. water and 47.57 gm. alcohol per 100 gm. solvent, and showed a lower critical temperature of 23.5°; i. e., it cleared on cooling to that temperature, and remained clear below it. Curious to see if another upper critical solution temperature would appear below this lower critical temperature, I cooled it to —10°, when the solution again became suddenly inhomogeneous, and the presence of an upper critical solution temperature could be plainly demonstrated at the same point as in the preceding case. After checking this point, the solution was heated past the lower critical temperature, and another upper critical temperature found at 57.6°. On account of lack of material of known purity these experiments

were not continued, but it appears that it is possible to have not only both an upper and a lower critical temperature in the same ternary mixture, as demanded by the theory of Timmermans, but also a second upper critical temperature which lies below the lower critical temperature, and does not appear to have been previously considered possible. It may have been caused by impurities in the alcohol, but that does not seem probable, and the phenomenon will be further investigated.

The effect of temperature upon the equilibrium in the case of propyl alcohol and sodium chloride is the largest of any of those here studied. At the close of the third series of determinations (table 11) the solution had a lower critical temperature of 23°. It was cooled and more alcohol added to saturate the solution at the lower temperature. Thus the same amount of salt (20.636 gm.) and water (184.539 gm.) which at 23° dissolved 19.113

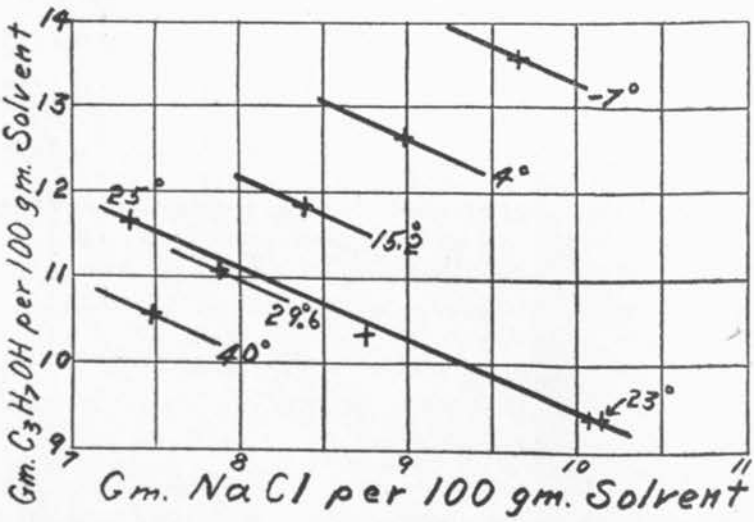

Figure 18. Isotherms in the System: Sodium Chloride, Normal Propyl Alcohol, Water.

gm. of absolute propyl alcohol was now able to dissolve 10.155 gm. more of the 98 per cent alcohol, and the solution had a lower critical temperature of —7°. By warming the solution and adding successive portions of water, solutions were obtained having lower critical solution temperatures of 4.0°, 15.2°, 29.6°, and 40.0°, and their composition has been plotted with the other solutions in figure 12, where it will be noticed that they form a line of considerable length. The composition of the solutions and their critical temperature of solution is shown in table 12, below, numbers 1 to 6, and the course of the isotherms at the various temperatures at that point indicated in figure 18.

Some experiments were also performed in solutions more dilute as to

salt and more concentrated as to alcohol, and both upper and lower critical solution temperatures obtained in the same solution in some cases. The solution at the start (no. 7, table 12) was the last one given in table 11; it had a lower critical temperature of 25.2°. By warming and adding successive portions of water and, at the last, of alcohol, the solutions numbers 8 to 11 in table 12 were produced. Care was taken to correct frequently

TABLE 12

No.	Composition, grams per 100 grams solvent			Critical solution temperature deg. C.	
	NaCl	H_2O	C_3H_7OH	Lower	Upper
1	10.128	90.61	9.39	23.0	Not determined
2	9.652	86.40	13.60	—7.0	Not determined
3	8.983	87.35	12.65	4.0	Not determined
4	8.394	88.18	11.82	15.2	Not determined
5	7.918	88.85	11.15	29.6	Not determined
6	7.498	89.44	10.56	40.0	Not determined
7	2.280	47.25	52.75	23.0	Not determined
8	2.271	47.46	52.54	25.2	Not determined
9	2.264	47.62	52.38	27.9	Not determined
10	2.254	47.85	52.15	34.0	40.0
11	2.253	47.88	52.12	35.7	35.7 (?)
12	2.209	46.97	53.03	32.1	42.8

for loss by evaporation, all the experiments being conducted in a flask with a rubber cork through which passed a standardized thermometer. As the cork must be frequently loosened to relieve the pressure, there was always a loss during heating. For this reason the calculation of the results is complicated, and only the final results are given in the table.

It will be noted that in the next to the last determination (no. 11), the upper and lower critical temperatures appear to have become identical. The

TABLE 13

Composition, grams per 100 gm. solvent					Critical solution temperature, deg. C.	
NaCl	d_1	Alcohol	d_2	Alcohol Corrected	Lower	Upper
2.280	0	52.75	0.00	52.75	23.0	....
2.271	9	52.54	.14	52.40	25.2	....
2.264	16	52.38	.26	52.12	27.9	....
2.254	26	52.15	.42	51.73	34.0	40.0
2.253	27	52.12	.43	51.69	37.5	37.5
2.209	71	53.03	1.14	51.79	32.1	42.8

solution from the previous test had been warmed a couple of degrees, and water added (0.150 gm.) to just clear the solution. The temperature was now 35.7°, and on cautiously warming, no cloudiness appeared. Cooling again produced at one point a possible trace of cloudiness, which immediately disappeared. This then appears to be at a point where the two critical temperatures coincide.

As the above table contains four variables, the relations it contains cannot be plotted as they stand. One variable is easily eliminated, for purposes of plotting, by expressing the table as above, and then plotting the composition of the solvent as one variable. If the percentage of alcohol be plotted as increasing from left to right, the percentage of water increases in a corresponding way from right to left, and both are represented by a single point. This simplification would make it possible to plot the effect of a change of temperature upon the solubility of the alcohol in a given salt solution as in figure 17, if we could reduce all the values in the table to the same salt

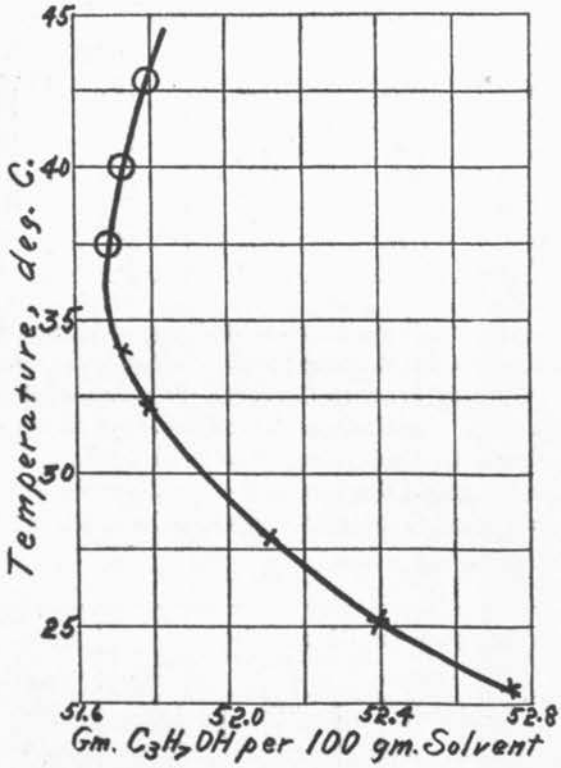

Figure 19. Upper and Lower Critical Solution Temperatures in the System: Sodium Chloride, Normal Propyl Alcohol, Water, at a Constant Salt Content.

content. All that we need to know for this purpose is the slope of the binodal curve at this point, (determination 7, table 12) but unfortunately this is not easy to determine accurately, as it is so steep that a small error will make a large difference in the results. By comparison with the next lower value (salt 3.686, alcohol 19.69 gm. per 100 gm. solvent) it would appear that over this range 0.406 gm. salt per 100 gm. solvent make a change of

33.06 per cent in the alcohol, or 0.081 per cent per milligram salt. In the other direction, taking the value for the upper layer at the quadruple point (salt 0.535, alcohol 88.28 gm. per 100 gm. solvent), and comparing with determination 7, we find that over this range a change of a milligram of salt gives an average change of 0.002 per cent alcohol. At the point in question, the value (slope of the curve) must lie between these two numbers. But the determination 12 in the table 12 gives us a check upon the approximate magnitude of the factor. It must be such that when applied to this determination, the corrected alcohol content lies between the corrected values for determinations 9 and 10, since the lower critical temperature of 12 lies between those of 9 and 10. By trial such a factor is easily found, and I have thus been led to assume that at the point on the binodal curve for 23°, represented by determination 7, table 12, a change of a milligram in the amount of salt per 100 gm. solvent causes a change of 0.016 grams alcohol per 100 gm. solvent. That is, since decrease of the salt content causes an increase in solubility of the alcohol, the observed value for alcohol is to be diminished by a value d_2 such that $d_2=0.016\ d_1$, where d_1 represents the difference (in milligrams per 100 gm. solvent) between the salt content of solution 7 and that of the solution which is to be corrected. In table 13 these corrections have been applied, so as to reduce all the observed solutions to the same basis as the original solution at 23°, and the value in the column headed "Alcohol, corrected," represents the solubility of alcohol, in grams per 100 gm. solvent, in a salt solution containing 2.280 gm. salt per 100 gm. solvent.

These values have been plotted in Figure 19, which thus represents graphically the effect of temperature upon the solubility of propyl alcohol in a solution of a constant salt content of 2.280 gm. per 100 gm. solvent. Here, as in the system: potassium carbonate, propyl alcohol, water, some of the upper isotherms coincide with lower ones.

SUMMARY

Six ternary systems of the class salt-alcohol-water have been investigated, and the complete curves for each worked out and drawn. In those which involve hydrated salts it is shown that the solubility of the salt is greater in absolute alcohol than when the alcohol is diluted with a small amount of water; in general the solubility is about the same in absolute alcohol as in 60 to 70 per cent alcohol.

A new method for the determination of ethyl alcohol has been worked out, and the results indicate that it is accurate in the presence of a small amount of methyl alcohol, if properly conducted.

It is shown for the first time that potassium fluoride has a very strong salting-out power for alcohols, and that its saturated solution is a better

drying agent than a saturated solution of potassium carbonate, as it has a lower vapor pressure. The anhydrous salt itself is a good dehydrating agent, and more rapid than potassium carbonate on account of its greater solubility in organic liquids, at least in the alcohols here studied. It is also unique among drying agents of its class in the large per cent of water it will take up to form its lowest hydrate.

A few experiments on the effect of temperature changes on the position of the binodal curve in the systems studied, show this influence to vary greatly in quantity. Both upper and lower critical solution temperatures were obtained in the same solution in several cases, and apparently in one of the systems there exists a second upper critical temperature below the lower critical temperature.

The salting-out powers of potassium fluoride were discovered jointly with Dean Geo. B. Frankforter of this University, and this thesis has been worked out under his supervision. I take pleasure in acknowledging my indebtedness to him for his interest and co-operation, and for many valuable suggestions, especially that of the use of the indicator in the determination of the binodal curve. Thanks are also due to the Minnesota School of Mines, who very kindly allowed me to use one of their calculating machines in the computation of the tables here given.

LIFE

Francis Cowles Frary, son of Francis Lee Frary and Jeanette Cowles Frary, was born in Minneapolis, Minnesota, July 9, 1884. He graduated from the Latin course at Central High School of Minneapolis in 1901, and entered the School of Chemistry in the University of Minnesota the same year. He received the degree of Analytical Chemist from that school in 1905, and the degree of Master of Science from the Graduate School of the University of Minnesota in 1906. He spent the winter and summer semesters of the year 1906-7 as a student in the University of Berlin and the Technische Hochschule in Charlottenburg, and has been enrolled as a student in the Graduate School of the University of Minnesota since that time. He was appointed Instructor in Chemistry in the University in 1905, and Assistant Professor of Chemistry in 1911.